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# Paleoenvironment of Coal and Its Relation to Drainage Quality

South Carolina Univ, Columbia Dept of Geology

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# PALEOENVIRONMENT OF COAL AND ITS RELATION TO DRAINAGE QUALITY

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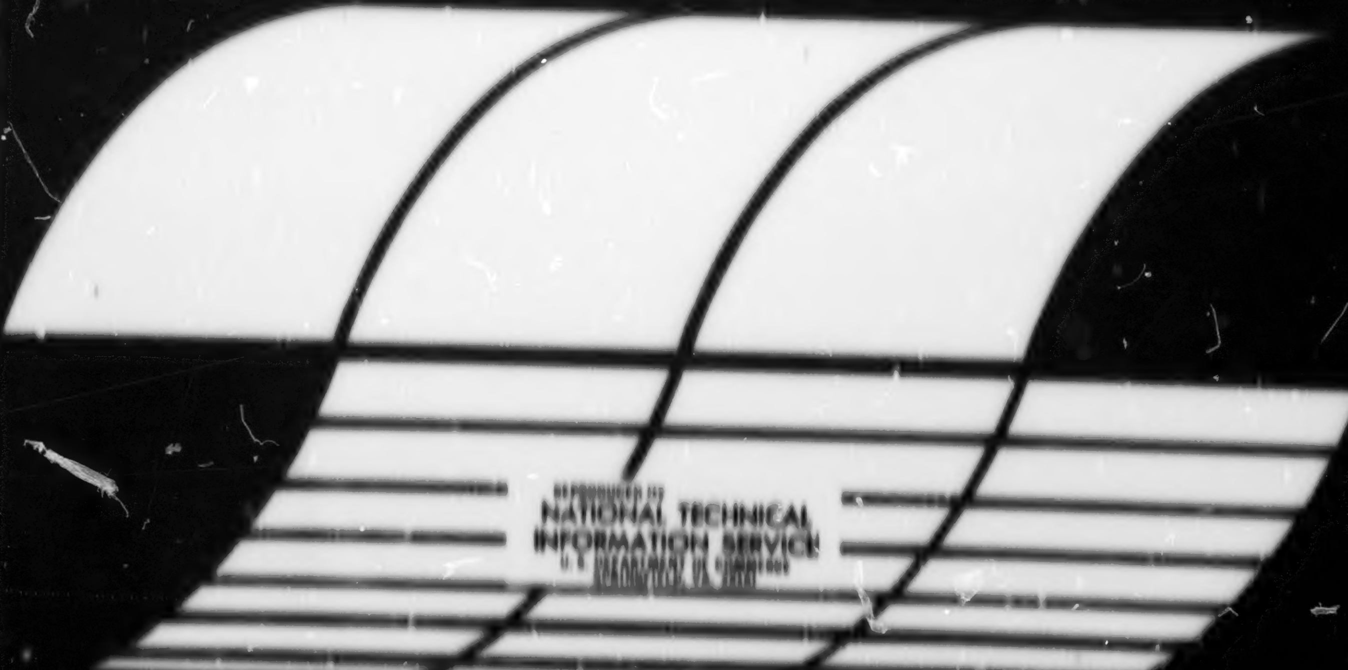

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The acid production potential of a coal was related to its paleoenvironment (environment of deposition) as interpreted from the overlying strata. Within the Appalachian coal field of eastern Kentucky, coals and associated strata were characterized as either back-barrier, lower delta plain or upper delta plain. Samples from various paleoenvironments were analyzed for sulfur content and pyrite types (reactive versus stable). Samples from the back-barrier, lower delta plain sequence had a relatively higher percentage of reactive pyrite than the seams within strata of upper delta plain. Both environments produced coals of similar total sulfur contents and both contained varying percentages of framboidal pyrite. Although reactive pyrite was present in seams of both paleoenvironments, a differing natural water chemistry caused acid mine drainage to be associated with the back-barrier, lower delta plain strata and never with the upper delta plain strata.

This study showed that the pyrite distribution and, more importantly, the water chemistry producing acidic or neutral drainages, were correlative with the paleoenvironment of the coals and associated strata.

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# FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

Reported here are the results of a study to develop a method whereby the quality of drainage expected from a mine located in a specific stratigraphic horizen can be approximated. Consequently, the data provided by this method can be utilized in the decision making process concerned with the economic benefits of resource extraction versus the degree of anticipated stream pollution and the cost of reclamation. This research will be of interest to both the mining industry and state and federal agencies associated with coal extraction. For further information contact the Extraction Technology Branch of the Resource Extraction and Handling Division.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

# ABSTRACT

The acid production potential of a coal was related to the coal's paleoenvironment (environment of deposition) as interpreted from the overlying strata. Within a triangular area between Hazard, Ashland and Grayson in the Appalachian coal field of eastern Kentucky, excellent rock exposures were afforded by a newly constructed highway system. The coals and associated strata were mapped to determine their paleoenvironment and characterized as either back-barrier, lower delta plain or upper delta plain.

Coals were sampled from various paleoenvironments and analyzed for sulfur content and distribution of pyrite types (reactive versus stable). The variability in the total sulfur contents of coal samples of uniformly distributed and geologically split seams was greater than expected. In the microscopic examination of coals, samples collected from the back-barrier, lower delta plain sequence contained a relatively higher percentage of reactive framboidal pyrite than the samples collected from seams within strata of upper delta plain. Both environments produced coals of similar total sulfur contents and both contained varying percentages of framboidal pyrite. Although reactive pyrite was present in seams of both paleoenvironments, a differing water chemistry caused acid mine drainage to be associated with the back-barrier, lower delta plain strata and never with the upper delta plain strata.

Water samples were collected from springs and seeps from the locales from which the coal samples were obtained and analyzed for pH, conductivity, sulfate, acidity and hardness. High sulfate-highly acidic, low buffered seeps, when present, flowed from strata of lower delta plain and some transitional sequences. High sulfate-neutral, highly buffered drainages emanated from strata of the upper delta plain. The presence of sulfate in water collected from all paleoenvironments indicates the presence of reactive pyrite in the sections, substantiating the results of the microscopic analyses.

For the area studied in eastern Kentucky, strata producing acidic drainages are characterized as having pyrite in the framboidal form and a paucity of a natural water buffering capacity. These rocks are associated with lower delta plain-back barrier sequences. On the other hand, strata which produce low to high sulfate-neutral drainages have relatively lower percentages of framboidal pyrite and are associated with highly buffered alkaline-water systems of alluvial-upper delta plain sequences.

This study showed that the pyrite distribution and, more importantly, the water chemistry producing acidic or neutral drainages, were correlative with the paleoenvironment of the coals and associated strata. Thus, it appears that mapping coals within the context of their paleoenvironment provides a tool that can be used to approximate the quality of drainage that can be expected from a proposed mining operation.

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# SECTION I

# SUMMARY AND CONCLUSIONS

## BACKGROUND

Iron disulfides ($FeS_2$) occurring either as marcasite or pyrite in the coal and associated strata are exposed to the atmosphere during mining processes and readily oxidize to a series of hydrous iron sulfates. These sulfate compounds are soluble in water and produce mine drainages that commonly have a pH in the range of 2, contain acidities that range from 400-2000 mg/l (as $CaCO_3$), iron concentrations of 50-500 mg/l (as ferrous iron), and sulfate contents in the range of 500-12,000 mg/l (as $SO_4$).

It has been shown by Caruccio (1968) that in coal mines of the Allegheny Group of Pennsylvania the degree of acidity is a function of (1) the calcium carbonate content of the strata (which produces a neutralizing medium), (2) the pH of the ground waters before mining (which controls the occurrence of the various types of "iron bacteria" that catalyze the acid producing chemical reaction); and (3) the mode of occurrence of the iron disulfide.

Iron disulfide occurs in coal strata as euhedral grains, coarse grained (greater than 25 microns) masses which replaced the original plant matter, coarse grained platy masses occupying joints in the strata, and framboidal pyrite. The latter occurs as clusters of spherical agglomerates comprised of 0.25 micron grains of iron disulfide and are finely disseminated throughout the coal and associated strata. Of these basic types of pyrite, it is only the last one, the framboidal type, that decomposes rapidly enough to produce severe acid mine drainage (Caruccio, 1970). The other types of iron disulfide decompose at relatively slower rates; the amount of acidity produced is generally low and can be neutralized by minor amounts of alkalinity produced by the calcium carbonate found in the rocks. Strata containing large amounts of "sulfur" occurring as framboidal iron disulfide will produce more acid than strata containing equal amounts of "sulfur" composed of coarse grained non-framboidal iron disulfide. Consequently, the severity of acid mine drainage pollution from coal mines is, in part, a function of the amount of framboidal iron disulfide in the rock sequence that is exposed to the atmosphere by the mining process.

The occurrence of the framboidal iron disulfide within a particular rock unit is correlative with the paleoenvironment of the stratum; i.e., the conditions under which the rock was deposited control the formation, deposition and occurrence of the framboidal iron disulfide. This association (framboidal pyrite related to certain paleoenvironments) is the key to identifying coal strata which when mined, will produce acid mine drainage pollution.

Contemporaneously with Caruccio's work, Ferm and his associates (Ferm et al., 1959), Ferm and Williams (1962, 1964, 1965), Ferm et al. (1967), Ferm and Cavaroc (1968), and Ferm (1975) were engaged in an extensive program of recognizing and mapping environments of coal deposition in the Appalachian coal field from Pennsylvania to Alabama. By comparing ancient coal bearing rocks to modern depositional analogues, a set of criteria has been developed for recognizing environments which range from alluvial plains through upper delta plain and lower delta plains grading into a tidally influenced back barriers and beach barriers. Applying these criteria to Caruccio's Pennsylvania data, the coals and associated rocks rich in framboidal pyrite would be recognizable as back barrier and lower delta plain deposits and strata with relatively less framboidal pyrite would be associated with upper delta and alluvial plain settings.

Because many Appalachian coal beds are known to represent several different environments in different places, and because others can be recognized as belonging to at least two environments, a criterion appears to be available for predicting the occurrence of framboidal pyrite without costly and time consuming analytical procedures. Strata and coals of varying paleoenvironments could be mapped (in both vertical and horizontal distributions) and zones rich in framboidal pyrite delineated. Having constructed these maps, areas can be identified that would, in advance of the active mining stage, delineate mines that would create major and minor environmental impacts from acid mine drainage pollution.

## METHODOLOGY

A triangular area within the Appalachian coal field of eastern Kentucky (between Hazard, Ashland and Grayson) was selected for study because of the excellent rock exposures afforded by the newly constructed highway system. From these exposures, paleoenvironmental profiles were constructed and samples of coals of the various depositional environments of coals could be sampled. Samples of coals collected along the Daniel Boone Parkway in the Hazard area and along I-64 in the Ashland-Grayson area were processed and analyzed for total sulfur. Representative sample splits were polished and examined by reflected light microscopy to ascertain the proportion of framboidal pyrite occurring in the sample.

Some of the samples were used in a laboratory experiment that was designed to test the acid production potential of coals from various paleoenvironments. Selected samples of coals were crushed to uniform sizes to standardize the surface area between samples. The samples were weighed and placed in plastic chambers where humidified air continuously passed over the samples. Periodically the samples were flushed with de-ionized water, the effluent volume recorded and hot acidity determinations were made on an aliquot of leachate. Acidity values were then adjusted to a common base and expressed as milligrams of hydrogen produced per 100 grams of sample. Cumulative acidity generated by each sample over a time period was then calculated and related to the acid production potential of coals representative of a particular paleoenvironment.

In a field geochemical survey, water samples were collected from springs and seeps emanating from the coal faces from which the coal samples were collected. Because the quality of ground water reflects the overall geochemistry of the strata and samples a larger geologic regime, the analyses of specific chemical quality parameters would serve to corroborate the data obtained from the sulfur analyses and the pyrite morphology distribution studies.

## RESULTS

The field survey that was designed to test the variability of total sulfur occurring in channel and column samples of coal seams showed that the percentages of total sulfur contents varied to a greater degree than was expected. Sulfur percentages varied greatly between column and channel samples collected from coals that were uniformally distributed over great distances as well as those that were stratigraphically split.

Pyritic sulfur contents were calculated from total sulfur contents of individual samples. These data were adjusted to give an average value for the total seam. When values of seams were plotted within groups of coals of similar paleoenvironments, patterns emerged that showed framboidal pyrite to be associated with back barrier and lower delta plain sequences. Samples that were collected from seams within strata of upper delta plain were also noted to have a variety of pyrite types, including framboidal pyrite. A Chi Square test and one way analysis of variance test both showed that there were significant differences between the framboidal content of the marine-brackish water and fresh water paleoenvironments, the former having a greater proportion than the latter. Additionally, a significant difference in the total sulfur contents was noted between the samples collected along the I-64 (Ashland-Grayson) area and the ones from the Hazard area, the former having a greater total sulfur content than the latter.

The results of the leaching test showed that samples collected from the back barrier-lower delta plain sequences produced abundant quantities of acidity, whereas those from the upper delta plain did not. Fortuitously, acid producing samples used in the leaching test had higher pyritic sulfur contents than the neutral samples which had a paucity of sulfur. As a result, the lack of acid production could be attributable to the lack of pyrite and not directly related to the absence or presence of framboidal pyrite. This possibility precluded a strong correlation between acid production potential and paleoenvironment.

The ground water seeps that were collected from strata exposed in the highway cuts and mine faces were analyzed for pH, conductivity, acidity, hardness and sulfate. High sulfate-highly acidic seeps, when present, occurred in strata of lower delta plain and some transitional sequences. On the other hand, high sulfate-neutral drainages emanated from strata in the upper delta plain dequence. The fact that high sulfate drainages flow from both types of strata suggests that reactive framboidal pyrite is present in strata of both paleoenvironments, but, as indicated previously from the results of the microscopic analysis, with relatively smaller percentages of the reactive pyrite occurring in the upper delta plain sections, and relatively greater percentages of framboidal pyrite in the lower delta plain-back barrier sequences.

Field studies showed that within a regional framework, the natural waters of strata of a lower delta plain-transitional paleoenvironment do not have sufficient buffering capacity to offset the acidity produced. Conversely, the waters of strata of an upper delta plain paleoenvironment contain sufficient alkalinity to offset and neutralize the minor amounts of acidity produced by the smaller percentages of framboidal pyrite present.

For the area studied in eastern Kentucky, strata which produce acidic drainages are characterized as having most of the pyrite in the framboidal form and a paucity of a natural water buffering capacity and are associated with lower delta plain-back barrier sequences. On the other hand, strata which produce low to high sulfate-neutral drainages also contain framboidal pyrite but are associated with highly buffered alkaline-water systems in alluvial-upper delta plain sequences. Thus, the distribution of framboidal pyrite, in combination with the concentration of alkalinity of natural waters, determines the quality of drainage from various strata. This study showed that both of these parameters were identified and correlated with the paleoenvironment of the coals. It appears, therefore, that mapping coals in the context of their depositional environments provides a tool that can be used to approximate the quality of drainage that can be expected from a mine sited in a particular stratigraphic horizon.

# SECTION II

# INTRODUCTION

## THE OCCURRENCE OF ACID MINE DRAINAGE

### Background of the Problem

The coal resources of the United States will undoubtedly play a major role in the future energy policy of this country. Various mining techniques available for the extraction of this energy resource from the ground disrupt the natural system and place various degrees of stress on the environment. In some cases, the mining process disrupts undisturbed rock strata and in addition to the physical disruption of the natural system, generates chemical imbalances which impose tremendous stresses on natural aqueous systems. The problem most prevalent and associated with coal mining in the bituminous coal fields of the eastern United States and one that has a major impact on the environment is the generation of acid mine drainage. One of the objectives in this study was to identify strata which have a high acid production capability and accordingly, predict the occurrence of acid mine drainage in advance of mining.

Acid mine drainage is, as the name implies, an extremely acidic, iron sulfate rich drainage that forms under natural conditions when certain coal seams are mined. When coal is mined, the iron disulfides, occurring either as marcasite or pyrite, which are commonly associated with the coal and overlying strata, are exposed to the atmosphere and oxidize in the presence of humidity and oxygen to form soluble hydrous iron sulfates. Subsequent natural water movement dissolves these compounds which chemically react to produce a highly acidic drainage with attendant high concentrations of iron and sulfate. Although this process is generally accepted as the mechanism by which acid mine drainage is formed, the exact chemical reactions are not fully understood.

Chemical reactions explaining the oxidation of the iron disulfide and the generation of acidity are given by the following equations:

$$FeS_{2(s)} + 7/2\ O_2 + H_2O = Fe^{++} + 2SO_4^{=} + 2H^+ \qquad (1)$$

$$Fe^{++} + \tfrac{1}{4}O_2 + H^+ = Fe^{+++} + \tfrac{1}{2}H_2O \qquad (2)$$

$$Fe^{+++} + 3H_2O = Fe(OH)_3(s) + 3H^+ \qquad (3)$$

$$FeS_{2(s)} + 14Fe^{+++} + 8H_2O = 15Fe^{++} + 2SO_4^{=} + 16H^+ \qquad (4)$$

Singer and Stumm (1968)

On the surface of a weathered coal mine face, yellow and white crusts commonly occur along certain horizons within the strata. These white and yellow salts are the oxidation products of the pyrite and are the crystallized products of equation 1. Some of the products have been identified as melanterite (white crystals of ferrous sulfate), copiapite (yellow crystals of ferric sulfate), halotrichite (white crystals of iron or magnesium sulfate), and alunogenite (white crystals of aluminum sulfate) (Lorenz, 1962).

The ferrous iron generated in the reaction described in equation 1 can be further oxidized to the ferric state in accord with equation 3 and generate additional amounts of acidity. It has been estimated by Stumm and Lee (1960) that a large part of the acidity generated in acid mine drainage production arises from the oxidation of ferrous iron to ferric iron. The ferrous and ferric hydroxides associated with the chemical reaction in equation 3 impart the red and yellow-orange color that is characteristic of acid mine drainage. The precipitated iron hydroxide is the "yellow boy" that is commonly observed in streams and coal mine areas.

## Factors Affecting Mine Drainage Quality

### Acidity (Sulfur as iron disulfide)

Sulfur in coal can occur as organic sulfur, pyritic sulfur or sulfate sulfur. Organic sulfur is that component which is incorporated in the plant structure and is organically bound within the coal. In general, the organic component is not chemically reactive. Sulfate sulfur usually represents the water soluble weathering products of the disulfides and in most cases constitutes a very small percentage of the total sulfur measured in a section. Pyritic sulfur is that sulfur which is found in the disulfide phase usually as either marcasite or pyrite.

Studies by Mansfield and Spackman (1965) have shown that variations in the total sulfur contents of coal samples collected from the bituminous coal field of western Pennsylvania, reflect variations in pyritic sulfur contents. In their study the organic sulfur content of a particular coal seam remained relatively constant from the top to the bottom of the seam. Although the values of organic sulfur varied from 0.5 to 2% between seams, variations in total sulfur content expressed variations in pyritic sulfur content within each seam.

In comparing two areas in central Pennsylvania, Caruccio (1968) showed that the occurrence of acid mine drainage produced in the strip mine areas could not be related to the sulfur content of the coals and overlying strata. The two areas in Pennsylvania, one containing strip mines that produced acid, while the other containing mines with non-acid drainages, had strata with total sulfur contents which varied and overlapped and whose values were apparently similar. Microscopic examination of polished samples of coal and rock strata collected from the non-acid producing area showed them to contain abundant amounts of pyrite as well as total sulfur percentages that were similar to the samples from the acid producing area.

In a combination of studies, selected samples of coal and rock were placed in leaching chambers and periodically flushed with distilled water. The quality of the leachate collected from each sample was analyzed and the degree of acidity produced by each sample ascertained. Representative splits of the samples used in the leaching chambers were analyzed for sulfur contents and equal portions cast in polished pellets for microscopic examination. Caruccio (1968, 1969) found that the pyrite morphology was significantly different between the samples that produced acid and those that did not, even though the total sulfur contents were similar.

In addition, there was a significant variation in the pyrite morphology between samples from the two areas of study. In samples from the non-acid producing area the pyrite commonly had a massive form and appeared to be secondary in origin. Most of the grains were greater than 400 microns and commonly had a morphology that suggested that the pyrite had replaced plant structures and occupied joints in the coal. In samples from the acid producing area, however, a major portion of the pyrite occurred as clusters of spheres measuring approximately 25 microns in diameter. Each of the spheres was an agglomeration of minute crystals of pyrite approximately 0.25 microns in diameter that collectively had a globular morphology. Gray, Shapiro and Coe (1963) called attention to this type of pyrite occurring in the Pittsburgh seam of Pennsylvania, which is called framboidal pyrite.

In terms of reactivity, Caruccio showed that framboidal pyrite is much more reactive and less stable than the massive secondary pyrite (1969, 1973). Samples containing framboidal pyrite when left in the lab were noted to readily decompose to produce the salt crusts that appear on the surface of the coals and which are products of the oxidation process. On the other hand, coarse grained particles of pyrite were noted to remain shiny and brassy for indefinite periods of time and did not show appreciable signs of weathering. Subsequent studies by Caruccio (1970) showed that the percentage of framboidal pyrite within samples of similar permeabilities, multiplied by the total pyrite content of that sample can be used as a measure of the acid producing potential of that particular sample. In this manner, samples could have high amounts of pyritic sulfur but if occurring as massive coarse grained secondary types will tend to remain stable and not produce acid. In contrast, if framboidal pyrite were to be present then it is expected to readily decompose and produce acid. On this premise, and in view of the natural limits of alkalinity imposed by the carbonate-bicarbonate geochemical reactions, the occurrence of acid mine drainage can be directly related to the occurrence of framboidal pyrite within a coal seam and associated strata.

## Alkalinity (Calcareous material)

The preceeding discussions show that the amount of acidity produced is a function of and dependent upon the amount of iron disulfide that is available for decomposition in the presence of oxygen and ferric ion (Smith and

Shumate, 1970). Given a fixed amount of oxygen and ferric ion it then follows that coals and strata containing high amounts of framboidal pyrite will produce highly acidic mine drainages. However, Caruccio and Parizek (1967) and Caruccio (1968, 1969) have shown that the degree of acidity is also a function of the calcium content of the strata (which has the potential of generating an alkaline, highly buffered and potentially neutralizing drainage); and the pH of the ground water before mining takes place (which controls the occurrence of the various types of iron bacteria that catalyze the acid producing chemical reaction). With regard to the latter, it has been shown that certain types of iron bacteria can oxidize the soluble iron from the divalent to the trivalent state, thereby further hydrolyzing the iron with an accompanying increased acidity (Anon., 1971).

Each of the factors mentioned above plays a major role in determining the quality of mine drainage that can be expected when a particular stratum is disturbed. In turn, the occurrence of these factors has been related to the depositional environment (paleoenvironment) of the coal and accompanying strata (Caruccio, 1968). In so doing, an association has been established between the paleoenvironment of the coal and the gross quality of drainage that can be expected from that seam.

Within a particular strip mine, numerous strata of varying paleoenvironments are uncovered by the mining process and the quality of the drainage emanating from that mine will be a blend of all the different chemistries produced by each rock type. Smith and his associates (1974) have developed a technique that evaluates the acid-base account of various overburden materials which can be used for selected material placement. Their technique is useful in the planning of overburden management through the identification of alkaline and acid producing strata. The present study, however, was restricted to and examined in detail the association between the occurrence of various modes of pyrite and the paleoenvironment of the coal as identified by the overlying rock types.

Of the hydrogeochemical factors controlling the quality of mine drainage, calcium carbonate occurring in the strata overlying a coal can generate moderate amounts of alkalinity. At a certain partial pressure of carbon dioxide occurring within the infiltrating waters that come in contact with the calcareous materials in the ground water regime, the amount of alkalinity (which is a function of the partial pressure of carbon dioxide) is limited by the solubility of the carbonate phase at a particular pH value. Within broad ranges and the geochemical limits of the carbonate solubility, the neutralizing capability of water passing over calcareous materials in the rocks overlying a particular coal has a maximum potential. Consequently, although the alkalinity produced within the ground waters has the potential to neutralize the acid mine drainage, the overall neutralizing effect is limited by the maximum alkalinity that can be possibly generated within the geochemical systems of the overburden material.

In the areas of the bituminous coal field of Pennsylvania which are overlain by calcareous glacial drift, alkalinities of infiltrating waters were measured as high as 460 milligrams per liter (as $HCO_3^-$) (Caruccio, 1968).

In some nonglaciated areas where the Allegheny and Pottsville formations crop out, the limited calcareous content of the rocks yields ground waters with alkalinities averaging around 75 to 150 mg/l (as $HCO_3^-$), which can effectively neutralize 1 to 2 mg/l acidity as $H^+$ or 100 to 200 mg/l acidity as $CaCO_3$. Given the limited amount of alkalinity that can be possibly generated in the stratigraphic section, the acidic quality of the mine drainage will be determined by the amount of acidity that is produced. If the acidity is less than the available alkalinity, the drainage will be neutral; if it is greater, the drainage will be acidic.

The pH of the ground water before the mining phase also reflects the occurrence of calcium carbonate in the overlying strata. In the absence of calcareous material within a stratigraphic section the pH of the natural ground water can be expected to be less than 5.5. Within this slightly acidic range the iron bacteria which catalyze the acid mine drainage reaction are noted to thrive and can effectively increase the amount of acidity produced. On the other hand, in the presence of calcareous material in the section, the ground waters can be expected to be alkaline which preclude the occurrence of acid producing bacteria and in some cases is conducive to the viability of bacteria that produce basic substances (Anon., 1971).

## THE ASSOCIATION OF ACID MINE DRAINAGE WITH THE DEPOSITIONAL ENVIRONMENT (PALEOENVIRONMENT) OF COAL AND STRATA

### Previous Studies

The occurrence of sulfurous materials in the stratigraphic section of western Pennsylvania has been outlined in a general way by Williams (1960) and Williams and Keith (1963). Williams (1960) documented a change of paleoenvironments within the Allegheny Group of upper Pennsylvanian age in the bituminous coal field of western Pennsylvania. He showed that the rocks and the coals at the base of the Allegheny Group contained fossils which were characteristic of a marine brackish water paleoenvironment. In general, the paleoenvironment of the rocks became more continental and fresh water toward the upper part of the Allegheny Group. Work by Ferm and Williams (1960) showed that the basal rocks that were deposited in a brackish water environment become more marine toward the western part of Pennsylvania.

Mansfield and Spackman (1965) traced the variation in the petrography and the composition of the coals in the lower part of the Allegheny Group (Lower Kittanning, Lower Clarion) up through the coals into the upper part of the Allegheny Group (Freeport seams) across western Pennsylvania. With the exception of one sample in the Lower Freeport coal, the coals, when viewed on a regional scale, became more sulfurous as the environment of deposition became more marine.

Williams and Keith (1963) statistically related the distribution of sulfur in coals to the occurrence of the marine roof rocks. By comparing the coals in the lower and the upper part of the Allegheny Group, they showed that coals capped by marine roof rocks had a greater sulfur content than the coals capped by non-marine roof rocks.

Because the amount of acidity was thought to vary directly with the pyrite content of the coals and associated strata, it would be expected that mines extracting coals from strata of a marine-brackish water paleoenvironment should produce more acid than those mines mining coals associated with strata of a fresh water paleoenvironment. However, although the strata become more sulfurous (reflecting increases in iron disulfide), it has been shown in the first part of this report that it is the type of iron disulfide and not the amount which is the critical factor in predicting the occurrence of acid mine drainage. Strata containing large amounts of "sulfur" occurring as framboidal pyrite will produce more acid than the strata containing equal amounts of "sulfur" composed of coarse grained non-framboidal iron disulfide. Consequently, the association of framboidal pyrite with certain paleoenvironments is the key to identifying coal strata which will produce acid mine drainage pollution when mined. According to this hypothesis, coals from the lower part of the Allegheny Group of western Pennsylvania, which are overlain by strata of marine or brackish water paleoenvironments, should be rich in framboidal pyrite and would explain the major occurrence of acid mine drainage in this area. On the other hand, coals in the upper part of the stratigraphic sequence, which are overlain by strata of non-marine paleoenvironments, should have a paucity of framboidal pyrite and should produce drainages which should be neutral or slightly alkaline.

## Prediction of Acid Mine Drainage Pollution Problems

Ferm and his associates (Ferm et al., 1959; Ferm and Williams, 1963, 1964, 1965; Ferm et al., 1967; Ferm and Cavaroc, 1968; and Ferm, 1975) have been engaged in an extensive geologic mapping program of recognizing and mapping the depositional environments of coal deposits found in the Appalachian coal field from Pennsylvania to Alabama. By comparing the characteristics of the ancient coal-bearing rocks to present day environments of deposition, a set of criteria has been developed which can distinguish and recognize various paleoenvironments in the Carboniferous rocks. These environments range from alluvial plains through upper delta plains and lower delta plains grading into back and beach barriers which are tidally influenced. (Detailed definitions and criteria for recognition will follow). Interpreting Caruccio's data of western Pennsylvania in light of Ferm's paleoenvironmental reconstructions reveals that the coals and associated rocks rich in framboidal pyrite are associated with the beach and tidally influenced back barriers and lower delta plain deposits. In contrast, rocks and coals with a paucity of framboidal pyrite are recognized as the upper delta plain and alluvial plain sequence. In addition, where Caruccio's samples represent environments ranging from lower to upper delta plains within a particular coal bed distributed across a broad geographic range, a significant variation in the proportion of framboidal pyrite is observable.

Consequently, because many Appalachian coal beds are known to represent several different paleoenvironments in different places and because other seams can be recognized as belonging to at least two environments, a criterion appears to be available for predicting the aerial distribution of framboidal pyrite without costly and time consuming analytical procedures. If the differing environments of coal deposition can be readily recognized and shown on maps, then a predictive model explaining and delineating the occurrence of framboidal pyrite will be readily available. Strata representing varying paleoenvironments could be mapped (both vertically and horizontally) and zones in framboidal pyrite could accordingly be predicted.

## Definition of and Criteria for Recognition of Various Paleoenvironments

The identification of various paleoenvironments in the Carboniferous stratigraphic section is based on the present day recognition of various counterparts in active deltas. This is exemplified by a diagrammatic representation of the various components of an active delta as shown in Figure 1. For further reference, the diagram also shows the paleoenvironments and stratigraphic position of the various coals used in this study.

The principal criteria for the delineation of depositional environments are readily distinguished in the coal-bearing portion of the Carboniferous of eastern Kentucky and will form the basis for the following discussions. In this study, these criteria were used to identify the paleoenvironments of the strata containing the coals that were sampled.

The lower delta plain deposits of eastern Kentucky have been described by Baganz and others (1975). These deposits are dominated by thick coarsening upward sequences of shale and siltstone. They range in thickness from 50 to 180 feet (15 to 55 meters) and in lateral extent from 5 to 70 miles (8 to 110 kilometers). Recent counterparts of these sequences are forming in interdistributary bays and prodeltas of modern lower delta plains.

In the lower portion of these bayfill sequences, dark gray to black clay shales are dominant with irregularly distributed limestone and siderite common, while in the upper part of these sequences, rippling and other current related structures are common, reflecting the increasing energy of the shallower water as the bay fills with sediment. Where the bays filled sufficiently to form a surface upon which plants can root, coals formed, whereas burrowed sideritic sandstones occurred where the bays did not completely fill, thus permitting organisms to rework the subaqueous surface.

This general coarsening upward pattern of interdistributary bays is frequently broken by tongues of coarse-grain detritus introduced by crevasse splays. Chemically precipitated iron carbonate commonly occurs in persistent bands or as large carbonate concretions up to 3 feet in diameter (1 meter) along bedding surfaces. These secondary siderite concretions formed and lithified early as the enclosing shales and siltstones were compacted around them.

The bayfill sequences commonly contain marine and/or brackish water fossils and burrow structures. They are usually most abundant in the basal clay shales but also may occur throughout the sequence.

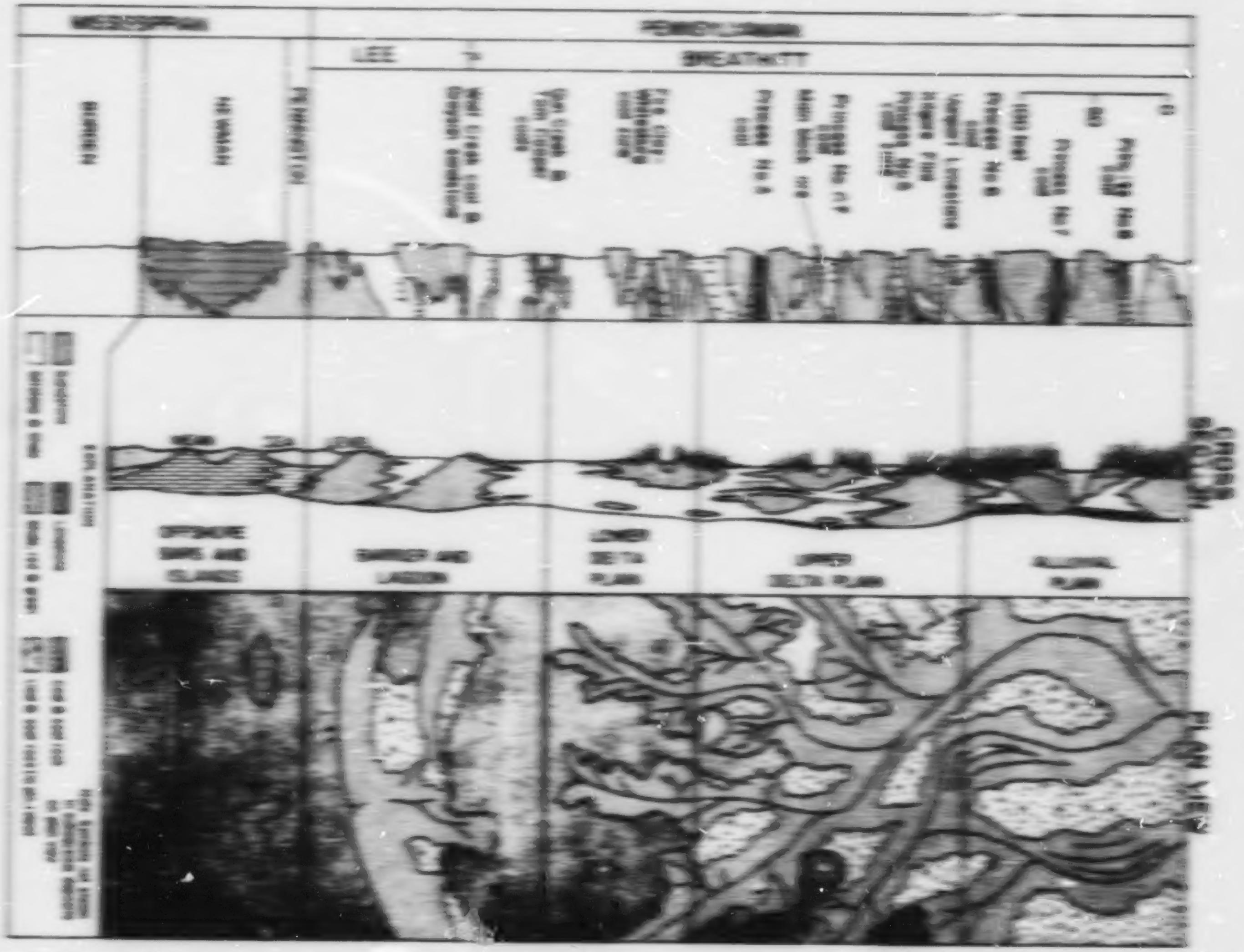

MISSISSIPPIAN
PENNSYLVANIAN
LEE
BREATHITT
0
50
100 feet
Princess No 8 coal
Princess No 7 coal
Princess No 6 coal
Vanport Limestone
Kilgore Flint
Princess No 5 coal zone
Princess No 4? coal
Main block ore
Princess No 4 coal
Fire clay; Whitesburg coal zone
Gun Creek & Tom Cooper coals
Wolf Creek coal & Grayson sandstone
PENNINGTON
NEWMAN
BORDEN
CROSS SECTION
PLAN VIEW
ALLUVIAL PLAIN
UPPER DELTA PLAIN
LOWER DELTA PLAIN
BARRIER AND LAGOON
OFFSHORE BARS AND ISLANDS
EXPLANATION
Sandstone
Siltstone & Shale
Limestone
Shale red & green
Coal & coal rock
Coal & coal rock in plan view

Figure 1. Diagrammatic representation of the carboniferous rocks and their depositional environments between Ashland and Olive Hill, Kentucky.

Overlying and laterally equivalent to the bayfill sequences are lithic greywacke sandstone bodies one to three miles wide (1.5 - 5 kilometers) and 50 to 80 feet thick (15 - 25 meters). Recent counterparts of these deposits are forming at the mouths of distributaries in modern lower delta plains. These distributary mouth bar sandstones are widest at the base and have gradational lower and lateral contacts. Grain size increases upward in the sequence and toward the center of the bar. Persistent graded beds are common on the flanks of the bars as are rippled surfaces (oscillation and current), whereas multi-directional festoon cross-beds are prevalent in the central portion of the bar. In this area of the bar, there is little lateral continuity of beds due to multiple scouring by flood currents. Slumps and flow rolls are associated with the flanks and front of the mouth bar where the sediment interface steepened beyond the angle of repose. Fossils and burrow structures are generally absent within the bar deposits, but where subaerial levees are constructed protecting the interdistributary areas from the rapid influx of detrital sediments, organisms return and burrow the flanks of the bar.

Distributary channels in the lower delta plain are characterized by two types of sedimentary fill: active and abandoned. Since channels in the lower delta plain are straight and exhibit little tendency to migrate laterally, except where they are deflected by underlying mouth bars, active channel fill deposits containing point bar accretion beds are not common. Where present, these deposits consist of sandy sequences up to 60 feet thick (18 meters) and 1000 feet wide (300 meters) which grade from coarse to fine upward with trough cross-beds in the lower part and ripple drift in the upper portion. The basal contact, which is scoured along an undulating or wavy surface, often truncates the underlying distributary mouth bar and bay deposits. Commonly pebble lag conglomerates occur at the base of the channel deposits as do coal spars which represent compressed pieces of wood or bark.

Due to the rapid abandonment of distributaries, fine-grained clay plugs are the predominant type of channel fill in the eastern Kentucky Carboniferous lower delta plain deposits. These abandoned fills are most often composed of clay shales and organic debris which settled from suspension in the ponded water of the abandoned distributary. In some cases, thick accumulations of coal-forming organic matter fill these holes. The clay shales are commonly root penetrated or burrowed. The only coarse-grained sediments occurring in the abandoned channels are thin rippled and small scale cross-bedded sands and silts which probably were deposited during floods or at sites near the distributary cut-off.

In the eastern Kentucky Carboniferous lower delta plain, levees are thin and poorly developed, the largest being about 5 feet thick (1.5 meters) and 500 feet wide (150 meters). Levees consist of poorly sorted, irregularly bedded, partially rooted, siltstones and sandstones. These beds have a pronounced dip (about 10 degrees) away from the associated channel. Coal beds, other than those associated with abandoned fills, are widespread but relatively thin.

In contrast to the thick fine-grained bayfill sequences of the lower delta plain deposits, the eastern Kentucky Carboniferous upper delta plain-fluvial deposits are dominated by linear, lenticular bodies of sandstone which, in cross-section, are 50' to 80' thick (15 to 25 meters) and 1 to 7 miles wide (1.5 to 11 kilometers). These sandstone bodies have a scoured base, sharply truncating the surface upon which they lie, but in the upper portion, they laterally intertongue with gray shales, siltstones and coal beds. The mineralogy of the sandstones very from lithic greywackes to arkoses, and the grain sizes are predominantly medium to coarse grained. Over the scoured base, the grain size diminishes upward in these sandstone sequences with abundant pebble lags and coal spar in the lower portions. Bedding in these sandstone bodies varies from massive beds with thick festoon cross-beds in the lower part which merge upward into point bar accretion beds (average dip of 17 degrees) containing smaller scale festoon cross-beds that are overlain by partially rooted sandstones and siltstones with climbing ripples. These characteristics, in addition to the lateral relationships, suggest a high energy channel flanked by swamps, small ponds, and lakes. The upward widening cross-sectional shape of the sandstone bodies and the point bar accretion beds indicate that meandering was important in the development of these deposits. These sandstone bodies have an en echelon arrangement suggesting episodes of lateral jumping of channels into adjoining backswamps.

Backswamp deposits consist of sequences, from the bottom up, of seat earth, coal, shale with abundant plant fossils and rare freshwater pelecypods, siltstone, sandstone, seat earth, and coal. The sandstone portion thickens laterally and merges with the major sandstone bodies. Thin 5 to 15 feet thick (1.5 to 4.5 meters) upward-coarsening sequences are typical deposits of open-water bodies, probably shallow ponds or lakes. The lateral extent of these deposits is only 1 to 5 miles (1.5 to 8 kilometers).

Levee deposits consist of poorly sorted, irregularly bedded sandstones and siltstones that are extensively rooted. They are thickest up to 25 feet thick (8 meters) near active channels and decrease in grain size and thickness away from the channels. The levee deposits also have a prominent dip (up to 10 degrees) away from the channel. Coals in the upper delta plain-fluvial deposits, locally, may be thick up to 32 feet (10 meters) but are laterally discontinuous (sometimes pinching out within 500 feet).

Lying between strata representing the lower and upper delta plain deposits of the eastern Kentucky Carboniferous is a transitional zone of rocks that exhibits characteristics of both the lower and upper delta plain sequences. The fine-grained bayfill sequences are thinner 5 to 25 feet thick (1.5 to 7.5 meters) than those of the lower delta plain, but they do contain marine to brackish faunas. Unlike the thin bayfill sequences of the upper delta plain they are extensively burrowed. Channel deposits exhibit features of lateral migration such as point bar accretion beds similar to the channels of the upper delta plain, but these transitional delta plain channels are finer grained than those of the upper delta plain. The levees associated with these channels are thicker 5 to 15 feet (1.5 to 4.5 meters) and more extensively root penetrated than those of the lower delta plain. Thin 5 to 15 feet (1.5 to 4.5 meters) splay sandstone are common in these deposits but are less numerous than in the lower delta plain yet more abundant than in the upper delta plain. Coals of the transitional delta plain are more laterally continuous than those of the upper delta plain and thicker than those of the lower delta plain.

The final major depositional setting of coal formation in the Carboniferous of eastern Kentucky is the lagoonal-back-barrier environment. The characteristics of this setting have been described by Horne, et al. (1974). The principal components of this environment are sequences of organic-rich dark gray shales and siltstones which are directly overlain by thin,laterally discontinuous coals or burrowed sideritic zones. These lagoonal-bayfills sequences coarsen upward, are extensively burrowed, and often contain marine to brackish faunas. Seaward, they intertongue with orthoquartzitic sandstones of barrier origin, whereas in a landward direction, they intertongue with subgraywacke sandstone of fluvio-deltaic origin. They are thick units 25 to 80 feet thick (7.5 to 24 meters) and similar to those of the lower delta plain, but are not as laterally continuous 3 to 15 miles (5 to 25 kilometers).

The intertonguing of the orthoquartzitic sandstones with the dark gray lagoonal bayfills is of three general types. First, long sheets of rippled or burrowed orthoquartzite dip gently (2 to 12 degrees) in a landward direction. Similar features to these are observed in modern barrier washovers into open water lagoons. The second type consists of wedge-shaped bodies that extend nearly horizontally in a landward direction for up to three miles (5 kilometers). Near the main body of orthoquarzite, they are up to 20 feet thick (6 meters) but rapidly thin and continue as nearly horizontal thin sheets ½ to 3 feet thick (1 meter). In the thicker portions of the orthoquartzites, bedding is predominantly planar to festoon cross-beds with amplitudes of 18 to 24 inches (45 to 60 centimeters) and a landward direction of dip. Similar features to these have been observed in flood tidal deltas in modern lagoons.

The third type of orthoquartzite intertonguing with the dark shales is tidal channel deposits that scour up to 40 feet (12 meters). These deposits may be associated with the inclined sheet sands or the wedge-shaped bodies, or they occur as solitary isolated units. Associated levees are either absent or inconspicuous. Near the main sandstone bodies, the orthoquartzites contain bimodal festoon cross-bedding, and grain size decreases upward. However, not all channels are filled with sandstone; most are filled with dark gray shales, siltstone, coal, or slump blocks.

The criteria for recognizing the various paleoenvironments as outlined above are summarized in Table 1 in their relative order of occurrence in order to facilitate a comparison of the various components.

|  | DEPOSITIONAL ENVIRONMENTS |  |  |  |  |
|---|---|---|---|---|---|
| CRITERIA FOR RECOGNITION | FLUVIAL AND UPPER DELTA PLAIN | TRANSITIONAL LOWER DELTA PLAIN | LOWER DELTA PLAIN | BACK-BARRIER | BARRIER |
| I. Coarsening upward |  |  |  |  |  |
| A. Shale and Siltstone sequences | C-R | C | A | C-A | R-C |
| 1. Greater than 50 feet | N | R-N | C-A | C-A | R-C |
| 2. 5 to 25 feet | R | C-R | C-A | C-A | R-C |
| B. Sandstone sequences | R-N | R-C | C-A | C | C-A |
| 1. Greater than 50 feet | N | N | C-A | N | C-A |
| 2. 5 to 25 feet | N | R-C | C-A | C | C |
| II. Channel Deposits |  |  |  |  |  |
| A. Fine grained abandoned fill | R | C-R | A-C | C | R-C |
| 1. Clay and silt | R | C-R | A-C | C | R-C |
| 2. Organic debris | R | C-R | A-C | C-R | R |
| B. Active sandstone fill | A | C | C-R | C-R | C |
| 1. Fine grained | C | C | C-R | C-R | C |
| 2. Medium and coarse grained | A | C-R | R | R | C-R |
| 3. Pebble lags | A | C | C | C-R | R-C |
| 4. Coal spar | A | C | C | C-R | R-C |
| III. Contacts |  |  |  |  |  |
| A. Abrupt (scour) | A | A | C | C | C-A |
| B. Gradational | C-R | C | C-A | C | C |
| IV. Bedding |  |  |  |  |  |
| A. Cross beds | A | C | A | A-C | A-C |
| 1. Ripples | C | C-A | A | A | A |
| 2. Ripple drift | C-A | C | C-R | R-C | R-A |
| 3. Festoon cross beds | A | A-C | C-R | C | C-A |
| 4. Graded beds | R | R | C-R | R-C | R-C |
| 5. Point bar accretion | A | C | R-N | R-N | R-N |
| 6. Irregular bedding | A | C | R-C | R-C | R-C |
| V. Levee Deposits | A | A-C | R-C | R | R |
| VI. Mineralogy of sandstones |  |  |  |  |  |
| A. Lithic graywacke | A | A | A-C | R | R |
| B. Orthoquartzites | N | N | R-N | A-C | A |
| VII. Fossils |  |  |  |  |  |
| A. Marine | N | R-C | C-A | A-C | A-C |
| B. Brackish | R | C | C | C-R | C-R |
| C. Fresh | C-R | R-C | R-N | N | N |
| D. Burrow structures | R | C | A | A | A |

KEY: A - Abundant, C - Common, R - Rare, N - Not Present

TABLE 1. CRITERIA FOR RECOGNIZING DEPOSITIONAL ENVIRONMENTS.

## HYPOTHESIS TO BE TESTED

Because of the association of framboidal pyrite with acid mine drainage and the association of framboidal pyrite with coals of strata of a particular paleoenvironment, the hypothesis which was postulated and tested in this study was concerned with predicting the occurrence of framboidal pyrite in the coal through the recognition of the depositional environment of the strata. If this hypothesis were true, stratigraphic sections can be mapped in advance of mining that would:

1) Identify the potential of acid mine drainage pollution associated with various coal seams.

2) For surface mined areas characterize strata which can be used for surface dressing as a substrate for vegetation in reclaiming the backfilled surface and those that will be potential acid producers and should be deeply buried and hydrologically isolated from the surface environment.

3) Identify coal seams by limits of high and low sulfur content and determine whether or not the high sulfur coals can be cleansed to produce low sulfur fuels. This is based upon the assumption that framboidal pyrite is fine grained and evenly disseminated within the coal and cannot be effectively separated from the coal by flotation processes. The fine grained pyrite is incorporated within the coal and floats off with the coal. On the other hand, coarse grained pyrite occurring as discrete particles readily affords a density variation within the coal particles and can be fractionated by flotation processes to produce a low sulfur coal.

To test whether an association exists between the paleoenvironment of a coal and the occurrence of framboidal pyrite, an area within the Appalachian coal field of eastern Kentucky was selected for study because of the excellent rock exposures afforded by the newly constructed interstate highway system. From these exposures, paleoenvironmental maps could be constructed and the environment of deposition of the coal readily identified. Having done so, samples of coals representing various paleoenvironments would be collected, processed and microscopically examined to determine the occurrence of framboidal pyrite.

As a further check on the validity of the data, water samples were collected from springs and seeps emanating from the coal faces from which the coal samples were collected. The quality of ground water reflects the overall geochemistry of the strata and the analyses of specific chemical parameters, reflecting particular geochemical reactions, would be used to complement the results of the microscopic study.

## SECTION III

## METHOD OF STUDY AND DATA PROCUREMENT

### AREA OF STUDY

Within a rough triangle formed by Olive Hill, Ashland and Louisa of the Appalachian basin of eastern Kentucky, an extensive interstate road building program had been actively taking place in the years 1971-1974. Because of the fertile farmland which occurs in the valley portion of that part of the state and because of the State's intent to preserve these agricultural areas, the new interstate highway system was projected and constructed through the mountainous areas. In so doing, extensive bedrock exposures were created and gave rise to spectacular road cuts, which in some cases averaged between 300-450 feet (100-150 meters) high and sometimes as much as a mile long (1.6 kilometers). These road cuts afforded excellent mapping control by which rocks and strata could be identified and paleoenvironment depositional features reconstructed. (See Figure 2).

In addition to the excellent exposures created by the newly constructed highway system in eastern Kentucky, the area was also chosen in anticipation of the future mining of the eastern Kentucky coal field. Most of the mapping information obtained in this study would also lend itself to future coal exploration programs and enhance coal mining and coal extraction from that part of the state.

The road cuts and exposures created by the highway construction presented the mapper with a three dimensional view by which to enhance his paleoenvironmental reconstructions. Sufficient opportunity to document the depositional environment of the coal and the overlying strata which were afforded by the road cut benches also lent themselves and provided an excellent mechanism by which to sample the coals. In most cases, the benches were created along the coal seams and consequently facilitated the sampling program.

### COALS

#### Method of Mapping

As a first step in mapping the strata on the large highway exposures, sequential overlapping photographs were taken of the outcrops to produce a composite photo mosaic of the exposures. Subsequently, a sufficient number of vertical sections were measured to encompass the lateral variability of the lithologies. Using the photo mosaics and measured sections, detailed

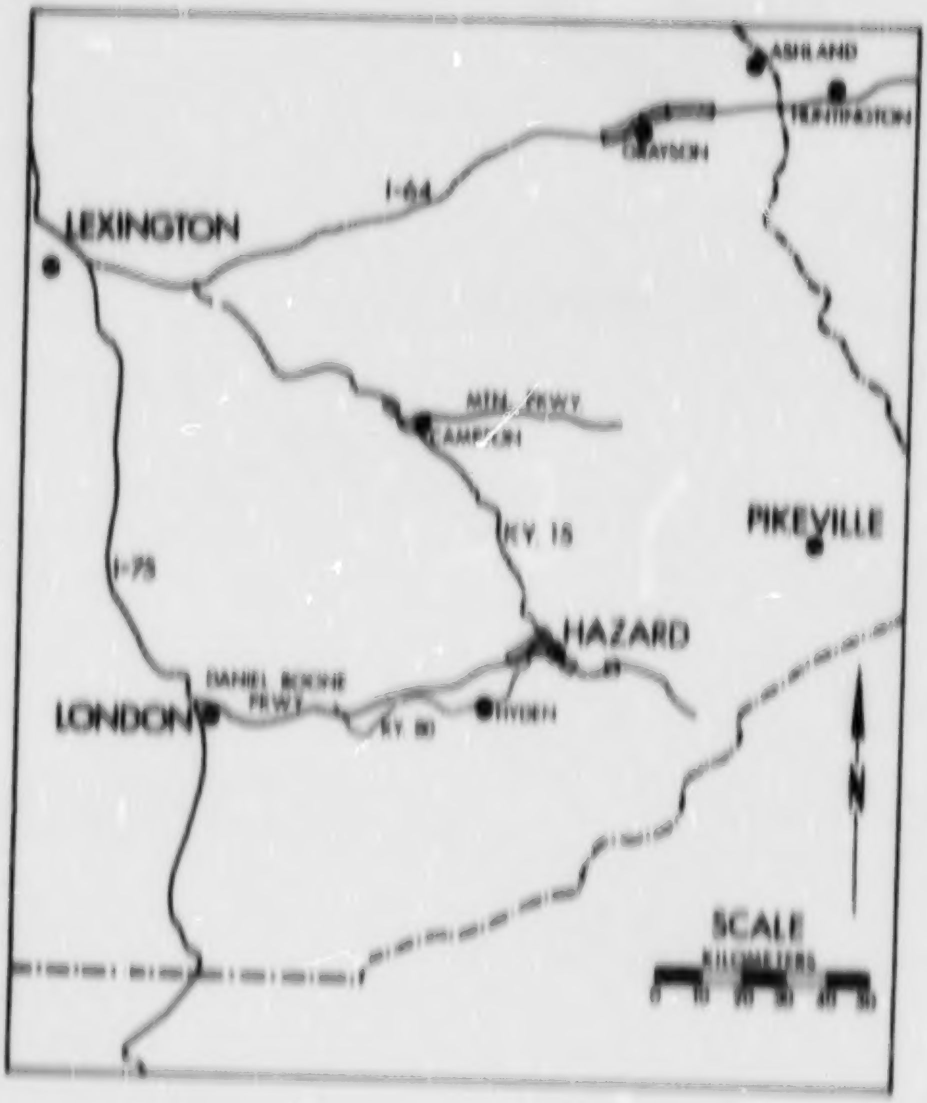

ASHLAND
HUNTINGTON
GRAYSON
I-64
LEXINGTON
MTN. PKWY
CAMPTON
KY. 15
PIKEVILLE
I-75
HAZARD
DANIEL BOONE PKWY
LONDON
KY. 80
HYDEN
N
SCALE
KILOMETERS
0 10 20 30 40 50

Figure 2. Location map of geologic cross-sections.

diagrams of the outcrops were prepared on graph paper. The outcrop diagrams were then generalized and replotted to a vertical scale of 1:240 and a horizontal scale of 1:6000 to show correlations and lithologic variations on a more regional scale along the trend of the direction of the highways.

## Method of Sampling and Depicting Data

After the outcrop diagrams were generalized and replotted along the highway trends, the paleoenvironment of each stratigraphic interval was ascertained using the criteria previously specified. At this stage of the reconstruction, the depositional environment of various strata and coals contained within the stratigraphic sequence could be identified. This guided the field sampling to selected areas where coals representative of particular paleoenvironments could be collected. Within each coal seam, sampling sites were randomly located at stations that were accessible, relatively dry, and where the coals appeared to be least weathered.

At each sampling location, the coal seam was examined to determine the degree of weathering. Badly weathered areas were avoided. In most cases relatively fresh samples could be collected by selecting appropriate locations along the coal seam. Thick coal seams were collected by column sampling the various physically different layers within the seams; i.e., blocky horizons, platy layers, massive, etc. If the seam was less than 12 inches (30.5 centimeters), then the entire seam was channel sampled. In selected areas where the coal seam was fresh and readily accessible, five stations approximately 75 feet (22.8 meters) apart were established, and samples were collected from various intervals to evaluate the lateral and vertical variations of sulfur content.

Before the start of the collection, the coal seam was dressed by using a shovel and pick to clear away the weathered surface. The thickness of the coal seam led the collector to either channel sample the entire seam or delineate various horizons for column sampling. Where pyrite rich layers were noted, special attention was paid to collecting samples and separate samples of pyrite concentrate were collected.

The samples collected from the coal face were bagged in plastic Zip-loc bags, labeled and shipped to the laboratory in South Carolina for analyses. All samples collected in the field were labeled by a code that identified the coal seam, the state in which the sample was collected and a specific site identification number that appears on the cross sections contained in this report.

The code has either three or four components separated by a slash which can be interpreted as follows:

The letter immediately preceeding the slash is either a K or an O depicting whether the sample was collected in Kentucky or Ohio, respectively.

Proceeding the K or the O is the identification code of the coal seam by explanations that appear in Table 2.

Following the slash is the collection site number which corresponds to the location on the cross section depicting the data. In some cases, a letter and/or number follows the site location number to show that multiple samples of the seam were collected at that sampling site.

On the cross section, below the code, appear the coal intervals that were sampled; "T" indicating Top, "M" for Middle, "L" for Lower, and "CH" for Channel Samples of the entire seam. At the bottom of each sample code the total sulfur percentage of that sample is shown. Because of the large numbers of samples that were collected, processed and analyzed, it was inevitable that some samples were lost. In this event, either the sample code is deleted or the analyses omitted from the station tag.

To complement the total sulfur analyses, many samples that were representative of the various paleoenvironments were selected for pellet fabrication for the microscopic identification of framboidal pyrite. During the course of examination, other varieties of pyrite were noted and the percentages of each were determined with a grid network that scanned the entire surface of the polished pellet. In addition, photomicrographs were taken of pellets characterizing features indigenous to the various paleoenvironments. These results will be discussed in the following section.

A summary of all samples collected and their codes, percentage sulfur and where applicable, percentages of various forms of pyrite, appear in Appendix A of this report. However, in order to facilitate the presentation, selected data representative of patterns and trends observed will be used as the basis for discussion.

## Analyses

Samples collected in the field were stored and transported to the laboratory in plastic Zip-loc bags that afforded an airtight seal which inhibited oxidation. The samples upon being unpacked, and in preparation for analyses, were hand cleaned to remove mud and other debris that was inadvertently collected with the sample. When the analysist was assured that all surface contamination was removed, the sample was crushed and processed according to the flow pattern illustrated in Figure 3. After the field sample was hand cleaned, it was crushed by a Chipmunk Jaw Crusher to pass 4 mm. The crushed sample was then riffled into two equal portions; one portion was sealed in a can under a nitrogen atmosphere. Nitrogen is injected throughout the crushed sample prior to sealing to prevent oxidation of the sample and preserve it for future studies. The sealed can is then clearly identified and stored in the coal repository at the University of South Carolina. The other riffled portion of the sample, which was to be used for the analyses, was further riffled into one portion which was to be used for the total sulfur analysis on the LECO and an equally representative portion which would be used for the fabrication of pellets.

TABLE 2. EXPLANATION OF COAL IDENTIFICATION CODES AND THE PALEOENVIRONMENTS REPRESENTED BY THE SAMPLES COLLECTED FOR THIS STUDY

| Coal | Identification Code | Area of Collection | Paleoenvironment Represented |
|---|---|---|---|
| Tom Cooper | TCK | Olive Hill, Kentucky | Lower Delta Plain |
| Fire Clay | FCK | Daniel Boone Parkway<br>Hazard, Kentucky | Upper Delta Plain |
| Lower Francis | LFRK | Daniel Boone Parkway<br>Hazard, Kentucky | Transition |
| Upper Francis | UFRK | Daniel Boone Parkway<br>Hazard, Kentucky | Transition |
| Lower Haddix | LHAK | Daniel Boone Parkway<br>Hazard, Kentucky | Upper Delta Plain |
| Middle Haddix | MHAK | Daniel Boone Parkway<br>Hazard, Kentucky | Upper Delta Plain |
| Upper Haddix | UHAK | Daniel Boone Parkway<br>Hazard, Kentucky | Upper Delta Plain |
| Hazard Six | HZ6K | Daniel Boone Parkway<br>Hazard, Kentucky | Upper Delta Plain |
| Hazard Seven | HZ7K | Daniel Boone Parkway<br>Hazard, Kentucky | Transition |
| Hindman Nine | HI9K | Daniel Boone Parkway<br>Hazard, Kentucky | Lower Delta Plain |
| Below Hindman Nine | BHI9K | Daniel Boone Parkway<br>Hazard, Kentucky | Lower Delta Plain |
| Princess Five | PR5K | Along I-64 near<br>Rush, Kentucky | Transition |
| Princess Five | PR5O | Ironton, Ohio | Transition |
| Princess Seven | PR7K | Along I-64 near<br>Rush, Kentucky | Upper Delta Plain |
| Princess Seven | PR7O | Ironton, Ohio | Upper Delta Plain |
| Wolf Creek | WCK | Along I-64 near<br>Rush, Kentucky | Back Barrier |

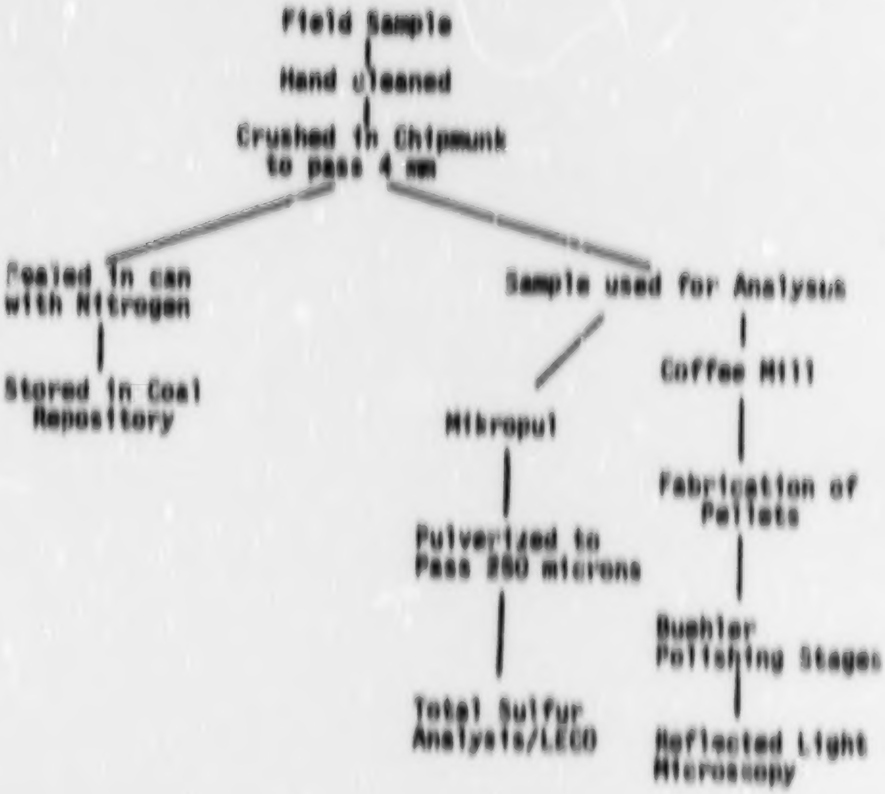

Field Sample
Hand cleaned
Crushed in Chipmunk to pass 4 mm
Sealed in can with Nitrogen
Stored in Coal Repository
Sample used for Analysus
Mikropul
Pulverized to Pass 250 microns
Total Sulfur Analysis/LECO
Coffee Mill
Fabrication of Pellets
Buehler Polishing Stages
Reflected Light Microscopy

Figure 3. Flow sheet for sample preparation and analysis.

The samples selected for the total sulfur analysis were pulverized using a Mikro-Pul pulverizer to pass a 200 micron sieve, air dried and stored in glass vials. During the analyses for total sulfur, a representative portion of the sample was withdrawn by rolling the jar and randomly collecting small increments of the pulverized sample to make up a 50 or 100 mg sample. The weighed sample was transferred to a porcelain crucible, augmented by a tin and iron accelerator and magnesium oxide flux, covered and ignited by a LECO induction furnace which converted the sulfur contained in the sample to sulfur dioxide. During this process the sample is covered by a purified oxygen gas flow which enhances burning and entrains the sulfur dioxide into a titration assembly which is colormetrically titrated to a particular end point by a starch-iodate reaction. The amount of titrant required to reach the end point is adjusted for blank corrections and an "F" factor and measures the percentage of total sulfur content of the ignited sample on a weight per weight basis.

The portion of the sample selected for microscopic examination was passed through a coffee mill grinder to pass a 2 mm sieve. The relatively large sample was further riffled to obtain a 10-15 gram portion which was air dried and stored in a glass jar in preparation for pellet fabrication. The sample was poured into a steel mold 3 inches (7.62cm) and exactly 1 inch (2.54cm) in diameter and stopped with a rubber plug. The sample was then covered with a low viscosity APCO 823 epoxy resin, stirred, cured, labeled and subsequently extruded by a hydraulic press. The pellets were mounted in Buehler sample holders and polished on a series of Buehler polishing wheels until a final polish utilizing a 0.05 micron alumina grit was achieved. The polished pellet surface can then be examined by an ore reflected light microscope to a magnification of 300X and the various pyrite morphologies readily identified. The microscope used in this study also had the capability of taking photo-micrographs of selected samples. When certain features, characteristic of particular samples were identified, appropriate photographs were taken and are included in this report.

## Water Chemistry of Coal Seeps

### Purpose

A major concern in this study was the rock-water quality interactions, in particular the effect that the aquifer composition and the occurrence of framboidal pyrite has on water quality. Samples of coal that were collected for analyses and used to approximate the occurrence and distribution of framboidal pyrite represent a small portion of the total coal seam under study. Efforts were made to collect representative portions of the seam from randomly located sample sites. When compared to the total volume of coal making up the coal seam, the sample volume is a small percentage of the total coal population.

Water seeps emanating from each coal, passed through the overlying strata, moved vertically into the coal seam and encountered the seat earth underlying the coal. This clayey layer inhibits the vertical migration of water and generally causes ground water to move laterally along the coal seam bed until the water emerges from the coal face. During the water's flow through the geological regime, the water must pass along joints and fractures and contact a variety of chemical constituents, including the framboidal pyrite.

Because the water reflects the gross chemical composition of the coal over a larger area, samples of water seeps emanating from coal faces were collected and chemically analyzed to complement the results obtained from the microscopic examination of the coal samples. In so doing, the results obtained from the microscopic examination of the pellets can be interpreted in conjunction with the water chemistry analyses to have a broader base and one of regional significance.

## Sample Collection

During the summer of 1975, water samples were collected from the areas from whence the various coal samples were collected. In so doing, water samples were collected from strata of the various paleoenvironments which could be used to evaluate the geochemistry of the water regime. At each location where the coals were sampled, the coal face was chiseled away with a hand pick until a water flow was encountered. In most cases, a slow, steady flow could be obtained and by the proper manipulation of a plastic straw, in juxtaposition with a sample bottle, a sufficient volume of water could be sampled for chemical analyses. Only in one or two cases did an insufficient flow preclude sample collection. Of the 48 coal sample locales, 46 had a sufficient water flow that was collected and subsequently analyzed. Each sample was analyzed for specific chemical parameters indicative of a particular chemical reaction and readily related to the geochemistry of the strata. The quality of the drainage could be used to relate pyrite stability or reactivity with the paleoenvironment of the strata. These data will further lend themselves to the interpretation of the results obtained from the microscopic analyses. The specific parameters measured and the reason for choosing them are outlined below.

## Chemical Parameters Measured

### pH

The pH, although not a quantitative measure of acidity, reflects the degree of acidity or alkalinity that could be expected from the sample. Within broad limits the chemical character of the sample could be quickly determined and related to the geochemistry of the strata. To insure that no subsequent changes in pH would occur due to changes in temperature, dissolution of gases, etc., all pH measurements were made in the field at the collection site using a portable Photovolt pH meter. Prior to measurement, the meter and electrode were calibrated using the appropriate buffer.

## Conductivity

Within broad estimates, the electrical properties of a solution reflect the ionic strength of that solution. Thus the conductivity of the water sample can be related to the total dissolved solid content of the water sample, and in a way approximates the chemical activity taking place within the aquifer or coal seam through which the ground water flows. Conductivities of samples were measured within a 12-hour period from time of collection using a portable Universal Interloc conductivity meter which was calibrated and standardized against a known conductivity standard solution. The conductivity measurements were also used to confirm the concentration of the total chemical species that were to be measured by conventional wet methods and to rapidly reconnoiter an area for water quality expectations.

Units of conductivity are commonly expressed as "micromhos per centimeter at T° C." Inasmuch as the definition of specific conductance already specifies the dimensions of a cube to which the specific conductivity measurements apply, the length in the unit is not necessary and may be omitted in practice (Hem, 1970). Accordingly, in this report the units of specific conductance may be expressed as micromhos.

## Acidity and Sulfate

The acidity of acidic drainages is assumed to develop principally from the hydrolysis of the oxidation products of pyrite. As outlined in the beginning of the report, the iron disulfide readily oxidizes to produce a ferrous sulfate compound which is readily soluble in water and hydrolizes to produce acidity and attendant amounts of sulfate. Accordingly, the measure of the acidity of water flowing from a seam can be related to the amount of reactive pyrite that could be expected to be found in that particular coal seam. These data coupled with the percentages of framboidal pyrite found in the seam, as noted to occur in the polished pellets, should give a total picture of the water quality that could be expected from a coal seam of a particular paleoenvironment.

The method of measuring acidity presented a problem, not because of analytical technique, but because of theoretical considerations concerning the definition of acidity. Many workers, in determining acidities, commonly titrate a water sample with a standard alkali solution to two endpoints, one at pH 4.5 which is defined as the "mineral acidity," and a second endpoint at pH 8.2, referred to as the carbon dioxide acidity (Sawyer, 1960).

Titrating a sample to these endpoints is meaningful if all the acidity is in the "free acid" form, that is, existing as sulfuric acid. However, if the acidity is in major part due to hydrolysis, which in fact is the case in acid mine drainage, then the acidity determined depends largely on the rate of hydrolysis and the oxidation state of the metal (Hem, 1970). To get a true picture of the total amount of acidity present in a sample, hydrolysis and the oxidation of the metals must be driven to completion before the sample is titrated. This is accomplished by boiling the sample before titration. In so doing, the dissolved carbon dioxide is driven off with the loss of carbon dioxide acidity, whereupon titration with a standard alkali gives the acidity due only to iron hydrolysis and free sulfuric acid, which is precisely the parameter of interest.

Generally, the endpoint is taken as 8.2 (phenolphthalein). Titration curves were determined for some samples collected in this study having varying degrees of acidities. In all cases an inflection point (which determined the endpoint of a titration) occurred near pH 8.3 which suggests this to be the proper endpoint.

Hot acidities were determined in a laboratory after boiling the sample for two minutes. This insured the complete oxidation and hydrolysis of the iron compounds and expelled the carbonic acid acidity. The sample was cooled to room temperature and titrated with a 0.0248N sodium hydroxide solution to a pH 8.3 endpoint which was potentiometrically determined (Rainwater and Thatcher, 1960).

The specific equations explaining the oxidation of pyrite and the generation of acidity were listed previously. The general equations governing the nature of the chemical reactions are repeated below to illustrate the relationship between acidity and sulfate and how sulfate anion concentrations can be used to substantiate the presence of reactive pyrite.

The oxidation of pyrite can be written,

$$FeS_2 + H_2O + 3\tfrac{1}{2}O_2 = FeSO_4 + H_2SO_4 \qquad (5)$$

The ferrous sulfate that is formed as an oxidation product may be oxidized further to ferric sulfate and dissolved in water as in equation (6).

$$Fe_2(SO_4)_3 \rightleftharpoons 2Fe^{+++} + 3SO_4^{=} \qquad (6)$$

The iron can hydrolyze as in equation (7)

$$Fe^{+++} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+ \qquad (7)$$

to form acidity and the iron hydroxides. The ferric iron formed during the acid-generating reactions further reacts with the available pyrite to form additional acidity, ferrous and sulfate ions as in equation (4).

From these reactions, it can be seen that the sulfate content is in part stoichiometrically related to the acidity. The relationship, however, is not linear because although the sulfate and iron arise from a common source, the acidity generated is a function of the oxidation state of the iron. However, within broad limits of acidity values, determined by the oxidation state of the iron, the acidity produced can be correlated with the sulfate content of water samples (Caruccio, 1968).

Because the acidity generated is a function of the oxidation state of the iron, it may be possible to have a sample whose acidity content increases with time as the iron is gradually oxidized. As a result, the solubility of the iron will decrease and unless the sample has a very low pH, the iron will precipitate out of solution. Inasmuch as the solubility of iron is pH-Eh dependent and the samples collected were exposed to atmospheric conditions prior to collection, determinations of iron content of the water samples were not performed. The delicate balance between ferrous-ferric ratios, pH-Eh relationships and the solubility of iron coupled with the rapid oxidation of ground water as it encounters a diffusion zone upon emerging from the rock or coal face, suggest that any interpretation of iron solubility data would in fact be tenuous. For these reasons, iron concentrations were not measured.

The sulfate content, however, remains constant assuming no significant dilution has taken place and the significance of sulfate measurements is obvious. The sulfate anion is the tracer of acid mine drainage and its presence can be used to approximate the degree of acidity present or that was present before neutralization took place. By analyzing the sulfate and acidity content of acid mine drainage from various sources, and plotting concentrations of sulfate against acidity, a range of acidity can be interpolated for a particular value of sulfate concentration. An assumption is made that all of the sulfate in the sample arises from the oxidation of pyrite. The lack of anhydrite or gypsum layers in the strata substantiates this assumption.

Precipitation of the sulfate ion is possible in the presence of high calcium waters. A water sample originally acid may be neutralized by calcium-bicarbonate rich waters, but because of calcium sulfate precipitation will contain a low sulfate content. An incorrect conclusion can be reached, namely, the sample never was affected by acid mine drainage. Calculations using sulfate and calcium concentrations of water samples analyzed in this study and solubility products for gypsum and anhydrite indicate that levels of sulfate concentration indicative of acid mine drainage contamination are possible even though precipitation takes place. Taking the least soluble phase of calcium sulfate, it was calculated that 1475 mg/l of sulfate anion would still remain in solution if precipitation occurred. Hence, the occurrence of pyrite decomposition can be interpreted through the presence of significant concentrations of sulfate anion.

Sulfate concentrations were analyzed by a modified barium chloranilate method outlined in Standard Methods for Chemical Analyses of Water and Wastes, 1971. The chloranilate ion is released in the presence of an acid buffer and develops a wine color that is proportional to the amount of sulfate ion present. The intensity of the color of the filtrate is colorimetrically measured on a B & L Spec-20 meter and related to a standard curve. To preclude cation interferences the samples were processed through ion exchange columns for ion removal before adding the reagent.

As noted previously, the decomposition of pyrite produces abundant amounts of sulfate, in addition to iron and acidity. In the absence of abundant amounts of either gypsum or anhydrite in the strata, it could be assumed that the primary source of sulfate in the water samples is the decomposition of reactive pyrite. As such, sulfate contents are an excellent measure of the degree of reactive pyrite present in the section.

### Hardness

Hardness is a measure of the inability of a water sample to produce suds in the presence of soap and is generally attributed to the occurrence and abundance of divalent cations. In water samples collected for this study, the hardness reflects the presence and degree of occurrunce of calcium, magnesium and iron. Water samples were analyzed for total hardness which grouped all divalent cations into one measurement. Selected cations were not specifically analyzed.

By examining the hardness data in conjunction with the acidity and pH data, the dominance of a particular cation could be accurately duduced. If, for example, a high hardness content of the water appears coupled with a high acidity and low pH, one can assume that the primary cation contributing to hardness is soluble iron. If, on the other hand, hardness is present in samples with a low acidity and high pH, it can be correctly assumed that the dominant divalent cation is calcium or magnesium.

Hardness determinations were made in the laboratory by the complexiometric EDTA method as outlined in Standard Methods (1971).

### Interpretation of Water Quality Data

The exact nature of the geochemical system of the coal seam and overlying strata from which the water sample was collected can be quickly ascertained if sulfate data are related to and examined in conjunction with hardness, acidity and pH. If, for example, a sample has high sulfate, hardness and acidity content, coupled with a low pH, it could be readily assumed that that particular stratigraphic section is generating acid mine drainage and contains abundant amounts of reactive pyrite. If, on the other hand, the sample contains low sulfate concentrations coupled with high hardness, low acidity and high pH, it could be assumed that the water flowed through strata containing calcareous material and a paucity of reactive pyrite. Finally, if a sample has high sulfate, high hardness, low acidity and high pH, it could be assumed that the geochemical system is such that acidity is being generated by reactive pyrite, but is subsequently neutralized by the alkalinity produced by calcareous material present in the section.

Thus, by noting the interrelationships between pH, conductivity, acidity, hardness and sulfate, the interrelationships and combinations thereof between reactive pyrite (generating acidity) and calcareous material (generating alkalinity) can be effectively determined. These data, used to complement the results obtained from the examination of the polished pellets, will be used in further discussions of this report. The wet chemical analyses of water samples collected in the field are shown in Appendix B.

## SECTION IV

## DATA AND INTERPRETATIONS

### VARIABILITY OF TOTAL SULFUR CONTENT OF COAL

### Varirbility Within Seams of Varying Paleoenvironments

To ascertain the degree of variability of total sulfur content that could be expected within coal seams of varying environments, the Princess Seven, Princess Five and Tom Cooper seams were selected for a detailed study; the former two were chosen as representative of the alluvial-upper delta plain environments, the latter representative of the back barrier environment. At specific locations within each coal seam sampling networks that extended vertically and laterally were designed to evaluate the total sulfur variation that could be expected within the seam.

Within the Princess Seven coal seam, three sampling techniques were used to collect samples within ± 6000 feet (2000 m) distance. At station PR7K/1, five column samples from the top to the bottom of the seam were collected and analyzed for total sulfur content. At location PR7K/2 the seam was sampled by halves and thirds at three sample stations located 1 inch (2.54 cm) apart from each other. Finally, at sample site PR7K/3, two channel samples of the entire coal were collected at stations one foot (30 cm) apart. The total sulfur contents of these samples appear in Table 3 and clearly show the marked vertical and lateral variation that could be expected in the total sulfur contents within a particular coal seam. See also Figure 4.

At station PR7K/1 the sulfur content varied from a low 1.31% in the bottom 5 inches (12.7 cm) horizon to a high of 6.54% in the 8 to 12 inch (20-30 cm) interval at the top.

At site PR7K/2 the central station had a sulfur content averaging 3.4% at the top half and a 1.26% at the bottom half of the seam. Stations 1 inch to the east and to the west of the central station at this locale had a high sulfur content occurring in the lower third of the seam and a low sulfur content occurring at the upper third of the seam; these data will be used in following sections and are included here to exemplify the points now being considered. At PR7K/3, channel samples taken at two locations had abnormally high sulfur contents, averaging between 6-7% total sulfur. These data point out that the total sulfur content can vary from as low as 1.1% to as high as 7.34% within a coal seam of one paleoenvironment.

From this preliminary study two observations regarding sulfur distribution are noteworthy. First, at the site PR7K/2, where samples were collected

### TABLE 3. TOTAL SULFUR PERCENTAGES OF SAMPLES COLLECTED FROM THE PRINCESS SEVEN COAL

| Code | Interval Sampled | Percentage Sulfur | Remarks |
|---|---|---|---|
| PR7K/1A | Top 8" (20 cm) | 2.38% | |
| PR7K/1B | 8" - 12" (20 - 30 cm) | 6.54% | Within one seam at one location |
| PR7K/1C | 12" - 22" (30 - 56 cm) | 1.93% | |
| PR7K/1D | 22" - 29" (56 - 74 cm) | 1.76% | |
| PR7K/1E | Bottom 29" - 34" (74 - 86 cm) | 1.31% | |
| PR7K/2 | T 1/3 | 3.46% | |
| PR7K/2 | M 1/3 | 3.33% | Samples PR7K/2, PR7K/2-W and PR7K/2-W were collected one inch (2.54 cm) apart |
| PR7K/2 | L 1/3 | 1.26% | |
| PR7K/2-W | T 1/3 | 1.13% | |
| PR7K/2-W | M 1/3 | 1.78% | |
| PR7K/2-W | L 1/3 | 4.13% | |
| PR7K/2-E | T 1/3 | 1.78% | |
| PR7K/2-E | M 1/3 | 1.44% | |
| PR7K/2-E | L 1/3 | 4.48% | |
| PR7K/3 | CH (1) 5" (13 cm) | 6.63% | Channel sample |
| PR7K/3 | CH (2) | 7.34% | Channel sample |

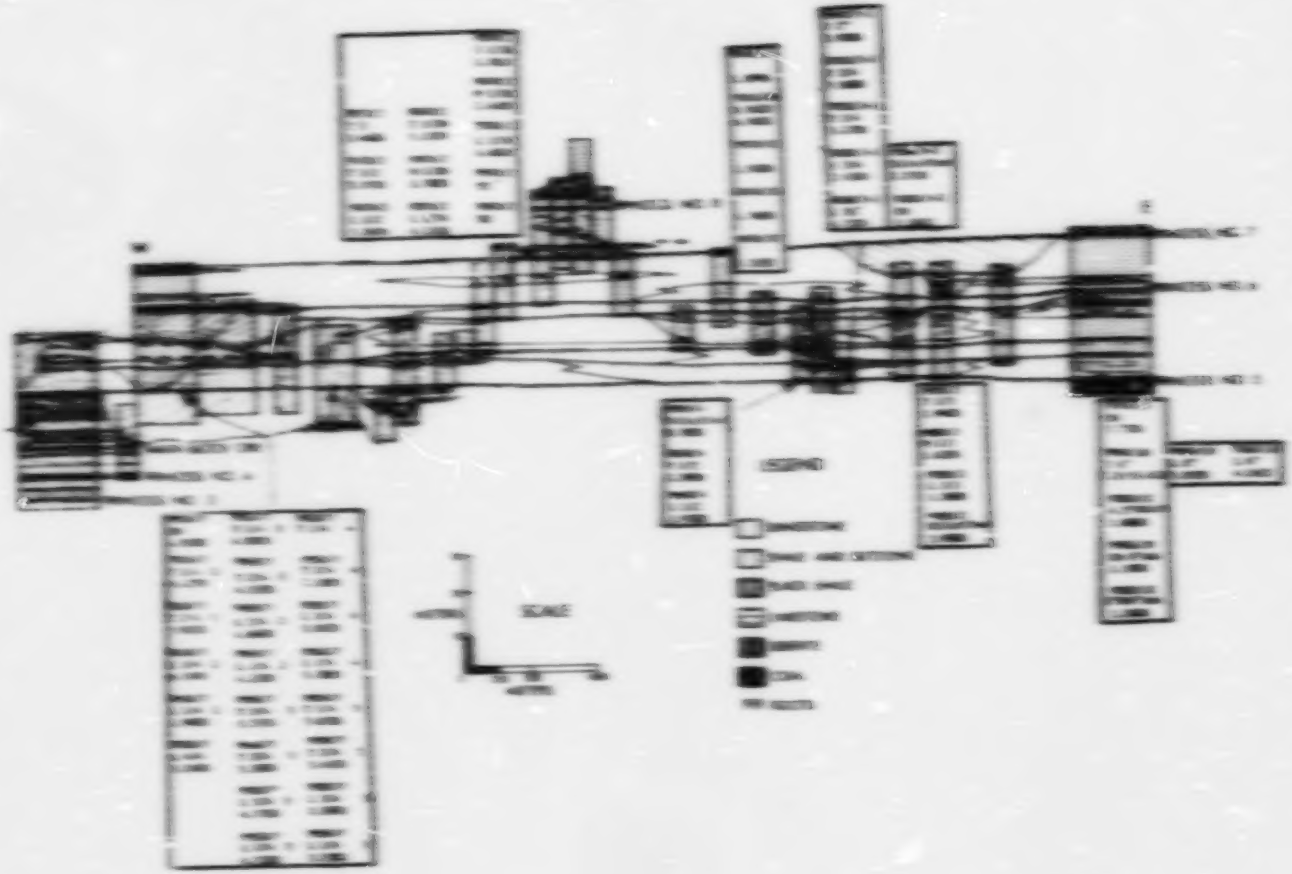


Figure 4. Geologic cross-section of Princess coals along I-64 near Rush, Kentucky.

from three locations within a 4 inch (10 cm) interval, there was no consistent pattern that could be used to predict whether high sulfur horizons will occur in either the top or the bottom of the seam. Second, the two channel samples collected at PR7K/3 contained total sulfur contents that exceeded the total sulfur contents of the individual samples which were parts of the seam that were collected at PR7K/1 or PR7K/2. Within these latter sample locations high sulfur contents were not found. Had channel samples of the coal seam been taken at PR7K/1 and PR7K/2, the high sulfur content layers of each of these separate samples would have been diluted by the lower sulfur horizons to produce a composite sample whose total sulfur content would have been even lower than the two channel samples. However, the total sulfur analyses of the channel samples collectud at the location showed that this was not the case and underscores the horizontal variability that could be expected along a seam.

Samples of coal were also collected from PR7K/5, PR7K/6 and PR7K/7 and analyzed for total sulfur content (Results appear in Appendix A). The results are summarized as follows:

| Sample | Percentage Sulfur |
|---|---|
| PR7K/5 | 0.36-0.73% |
| PR7K/6 | 1.61-3.5% |
| PR7K/7 | 2.06-5.63% |

On a regional basis, these data further illustrate the lack of correlation between the paleoenvironment and total sulfur percentages within the coal.

A cursory examination of the analyses of samples collected from the Princess Five (Figures 5-7) and the Tom Cooper (Figure 8) coals, representative of differing paleoenvironments, again shows a large variation in total sulfur content. Within the Princess Five coal seam (an upper delta plain coal), the total sulfur content varied from 1.2% to a high of 15%; whereas the Tom Cooper coal seam (a back barrier coal) had total sulfur contents which varied from 1.9% to 5.9%. These results showed that a tremendous variability in total sulfur content exists within coals of varying paleoenvironments and that a poor correlation exists between the total sulfur content of a coal and its depositional environment.

### Variability Within a Uniform Seam

To test the vertical variability that could be expected within a coal seam, column samples were collected from several locations in different seams. The distribution of sulfur within the Princess Seven at PR7K/7 is summarized as follows:

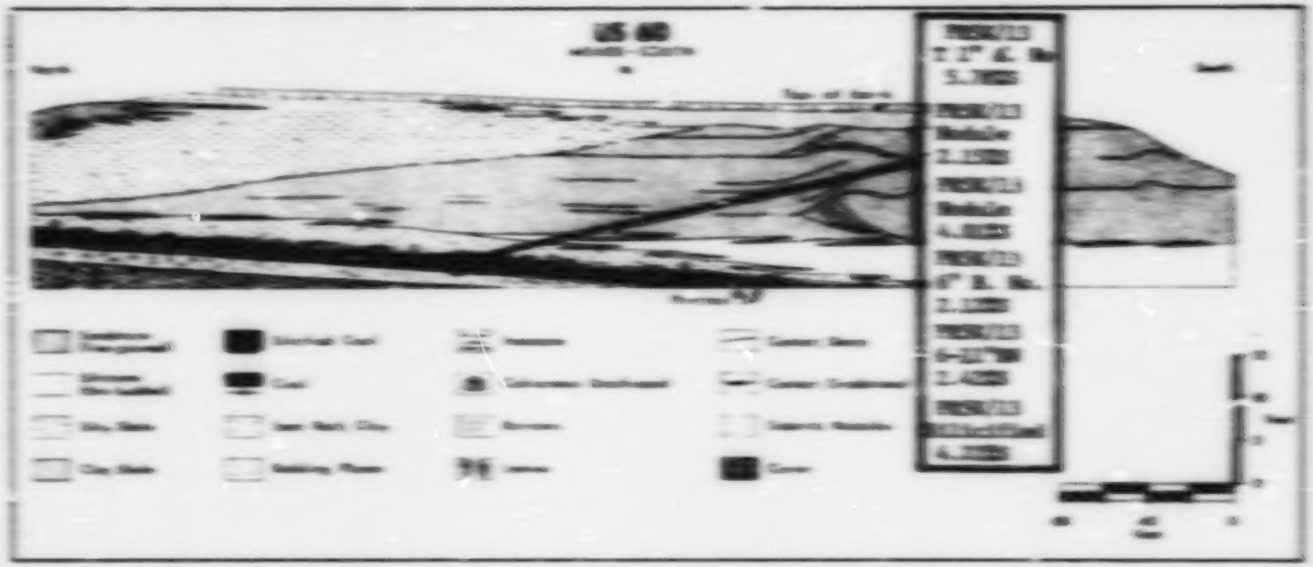

US 60
North
South

Figure 5. Geologic cross-section of the Princess Five coal along Kentucky 60 south of Meads, Kentucky.

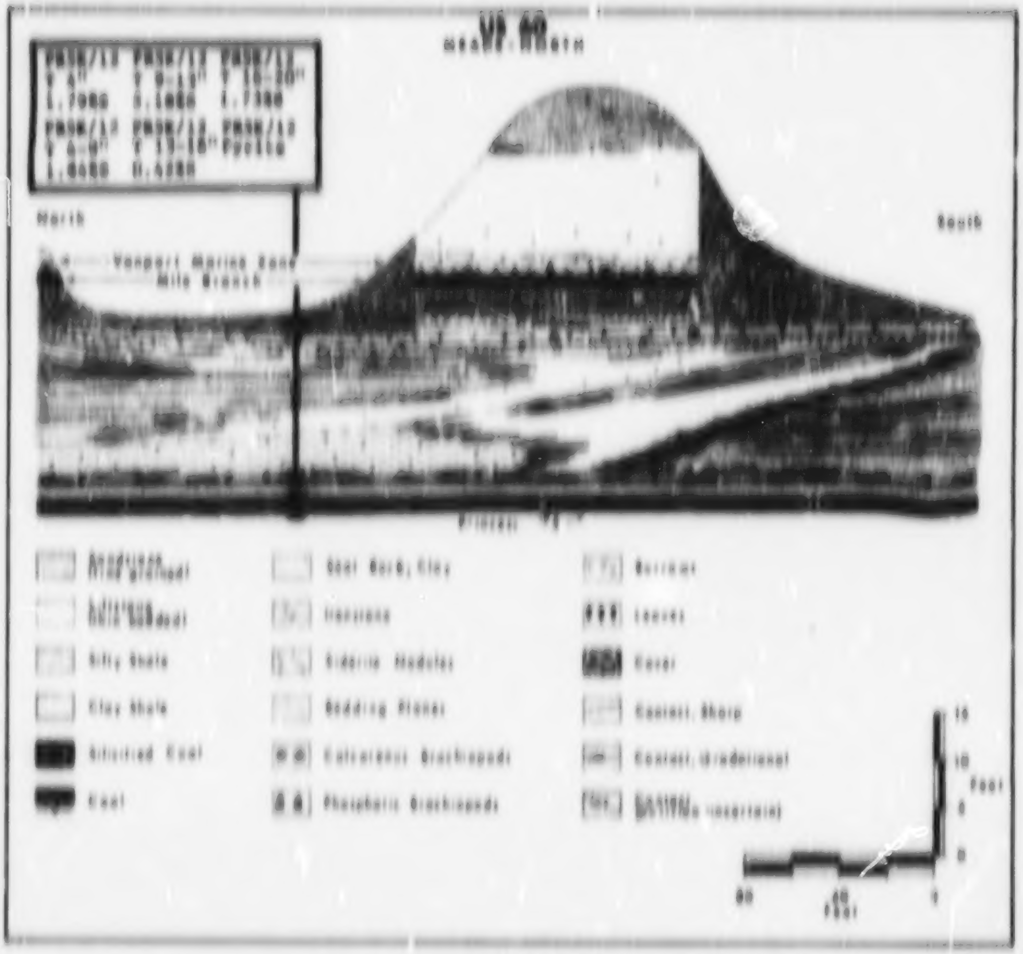

North
South
Vanport Marine Zone
Mile Branch
Silty Shale
Clay Shale
Coal
Siderite Nodules
Bedding Planes
Calcareous Brachiopods
Phosphatic Brachiopods
Leaves
Contact, Sharp
Contact, Gradational
15
10
5
0
Feet
Feet

Figure 6. Geologic cross-section of the Princess Five coal along Kenturky 60 north of Meads, Kentucky.

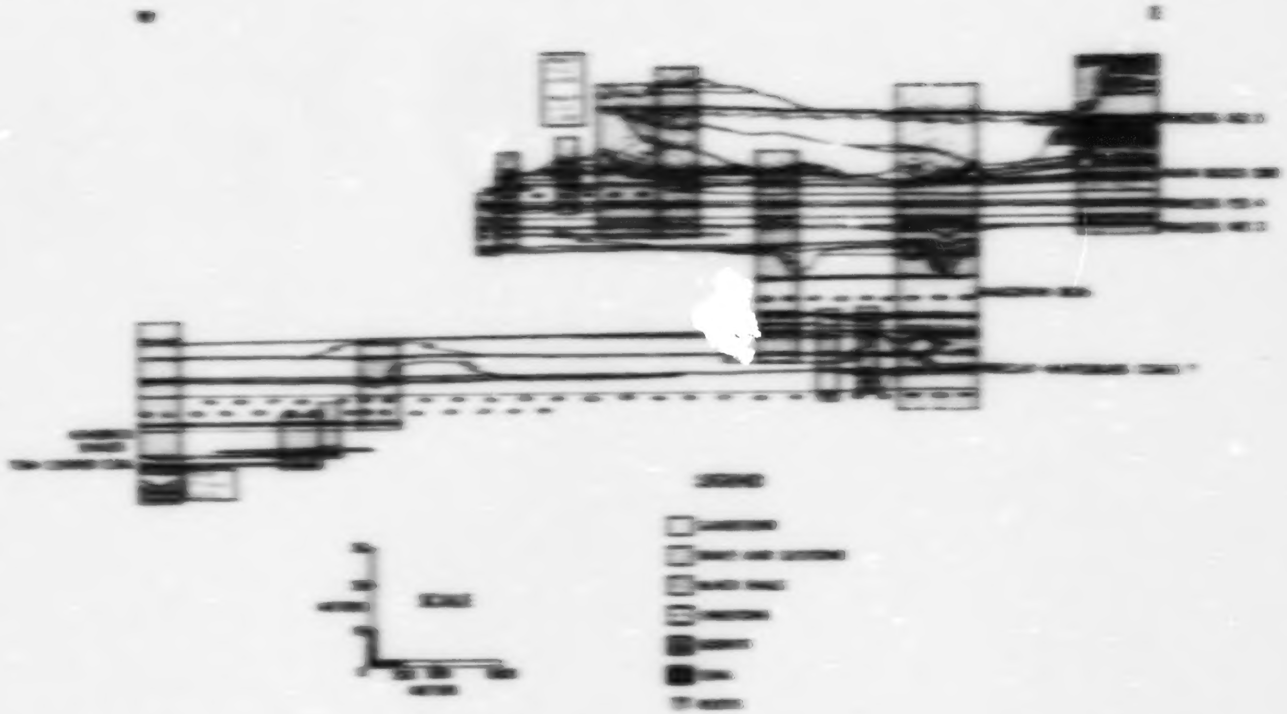


Figure 7. Geologic cross-section along I-64 near Grayson, Kentucky.

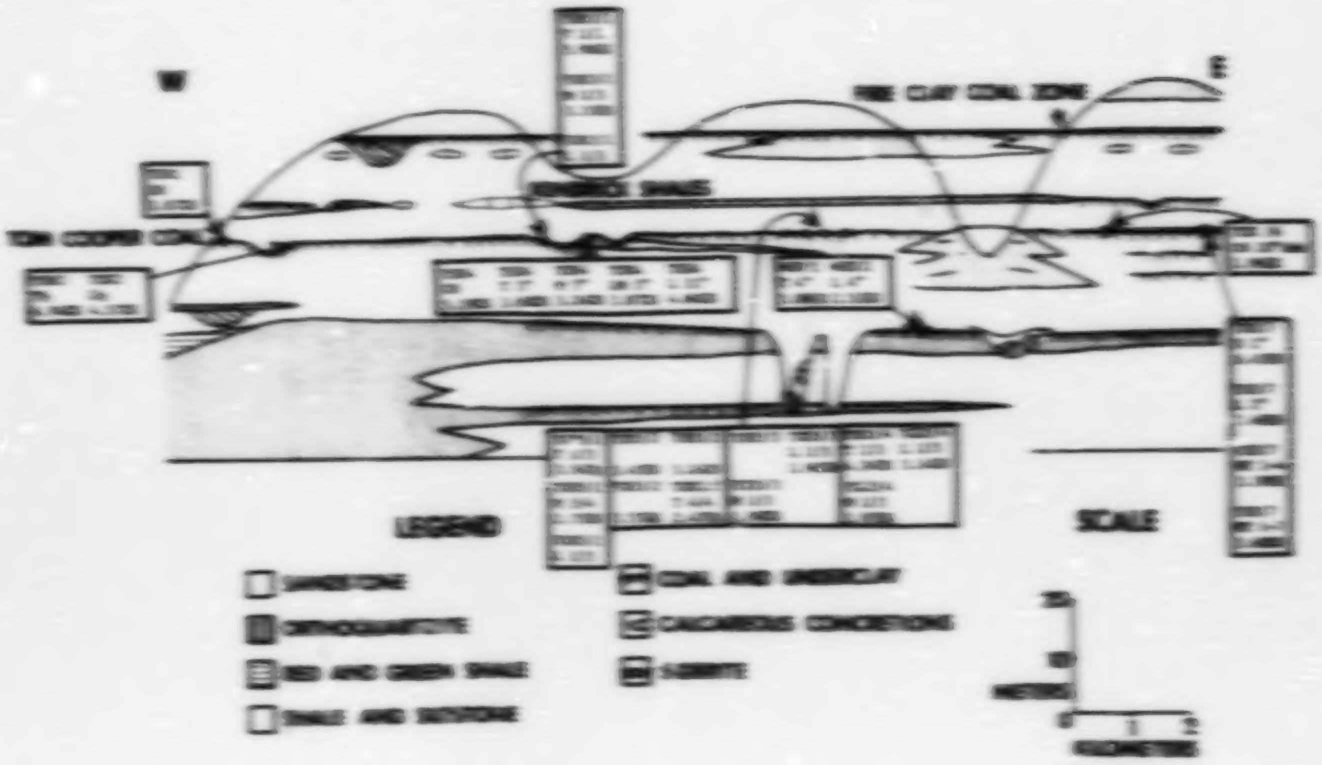

W
E
FIRE CLAY COAL ZONE
TOM COOPER COAL
LEGEND
SANDSTONE
ORTHOQUARTZITE
RED AND GREEN SHALE
SHALE AND SILTSTONE
COAL AND UNDERCLAY
CALCAREOUS CONCRETIONS
SIDERITE
SCALE
20
10
METERS
0
1
2
KILOMETERS

Figure 8. Geologic cross-section along I-64 near Olive Hill, Kentucky.

| Location PR7K/7 | Interval Sampled (Top to bottom) | Percentage Sulfur |
|---|---|---|
| | Top 7" (18 cm) | 5.63% |
| | 7 - 13" (18-33 cm) | 7.13% |
| | 13 - 20" (33-51 cm) | 2.06% |
| | 20 - 28" (51-71 cm) | 3.99% |
| | 28 - 36" (71-91 cm) | -- |
| | 36 - 41" (91-104 cm) | 2.56% |

Similar vertical variations in sulfur can also be seen in the Hazard coal seam. The analyses of samples collected at location HZ6K/19 are shown in the following summary (See also Figure 9).

| Location HZ6K/19 | Interval Sampled (Top to bottom) | Percentage Sulfur |
|---|---|---|
| | Top 4.5" (11.4 cm) | 0.55% |
| | 4.5 - 12.5" (11.4-31.8 cm) | 0.65% |
| | 12.5 - 18" (31.8-45.7 cm) | 0.59% |
| | 18 - 22.5" (45.7-57.2 cm) | 0.50% |
| | 22.5 - 25.75" (57.2-65.4 cm) | 0.71% |
| | 25.75 - 28.75" (65.4-73.02 cm) | 0.61% |
| | 28.75 - 31.75" (73.02-80.6 cm) | 1.86% |
| | Bottom 31.75 - 36.5" (80.6-92.7 cm) | 0.54% |

The examples cited above substantiate the trends and results that were found during the other phases of this study, that is - the vertical variations in total sulfur content within coal seams are greater than was previously suspected.

To ascertain the degree of horizontal variation of total sulfur content within a coal seam, three channel samples approximately 25 feet (7.6 m) were collected from the Princess Five coal at PR5K/10. These channel samples were analyzed for total sulfur content and had the following values: 3.06%, 4.14% and 3.74%. Although the variation was not as great as that found previously, it is apparent that the total sulfur content of channel samples within one coal seam can vary at stations along the seam.

To further evaluate the variation of sulfur content, three stations were located along the coal seam approximately one inch (2.54 cm) apart (PR7K/2, PR7K/2E and PR7K/2W). The data collected from the experiments at PR7K/2 and which appear in Table 3, are recombined and shown in Table 4.

TABLE 4. TOTAL SULFUR CONTENTS OF THIRD-COLUMN SAMPLES OF THE PRINCESS SEVEN COAL COLLECTED ONE INCH (2.54 cm) APART AT PR7K/2

| | PR7K/2W | PR7K/2 | PR7K/2E |
|---|---|---|---|
| Top Third of Seam | 1.13% | 3.46% | 1.78% |
| Middle Third of Seam | 1.78% | 3.33% | 1.44% |
| Bottom Third of Seam | 4.13% | 1.26% | 4.40% |

In addition, these results are plotted in Figure 10 which succinctly demonstrates the degree of lateral and vertical variability of total sulfur contents that could be expected within a coal seam.

In a final attempt to establish the vertical and horizontal variation that could be expected, an intricate sampling plan was designed along the Princess Five coal seam at station PR5K/7. At this locale, five stations numbered 1 through 5 were located about 20 to 80 feet (6.23 m) apart. The coal thickness varied from 6 to 9 inches (15-23 cm) and in spite of a relatively thin seam, which would have lent itself to a complete channel sample, one-quarter column samples were collected at each location (Figure 4). The results of the total sulfur analyses of the samples are shown in Table 5 and Figure 11, and further support the contention that large horizontal and vertical variations in total sulfur contents exist in a coal seam.

TABLE 5. TOTAL SULFUR CONTENTS OF QUARTER-COLUMN SAMPLES OF THE PRINCESS FIVE COAL COLLECTED AT PR5K/7

| Station | PR5K/7-1 | PR5K/7-2 | PR5K/7-3 | PR5K/7-4 | PR5K/7-5 |
|---|---|---|---|---|---|
| Coal Thickness | 7"(18 cm) | 6"(15 cm) | 6"(15 cm) | 9"(23 cm) | 7"(18 cm) |

Distance Between Stations 35 ft(11 m) 20 ft(6 m) 20 ft(6 m) 80 ft(24 m)

| Sulfur Content | | | | | |
|---|---|---|---|---|---|
| Top Quarter | 6.42% | 4.09% | 5.25% | -- | 3.67% |
| Upper Quarter | 3.98% | 4.52% | 5.26% | 7.10% | 3.41% |
| Lower Quarter | 6.59% | 4.08% | 4.77% | 3.04% | 2.29% |
| Bottom Quarter | 1.99% | 4.25% | 4.72% | 6.38% | 3.23% |

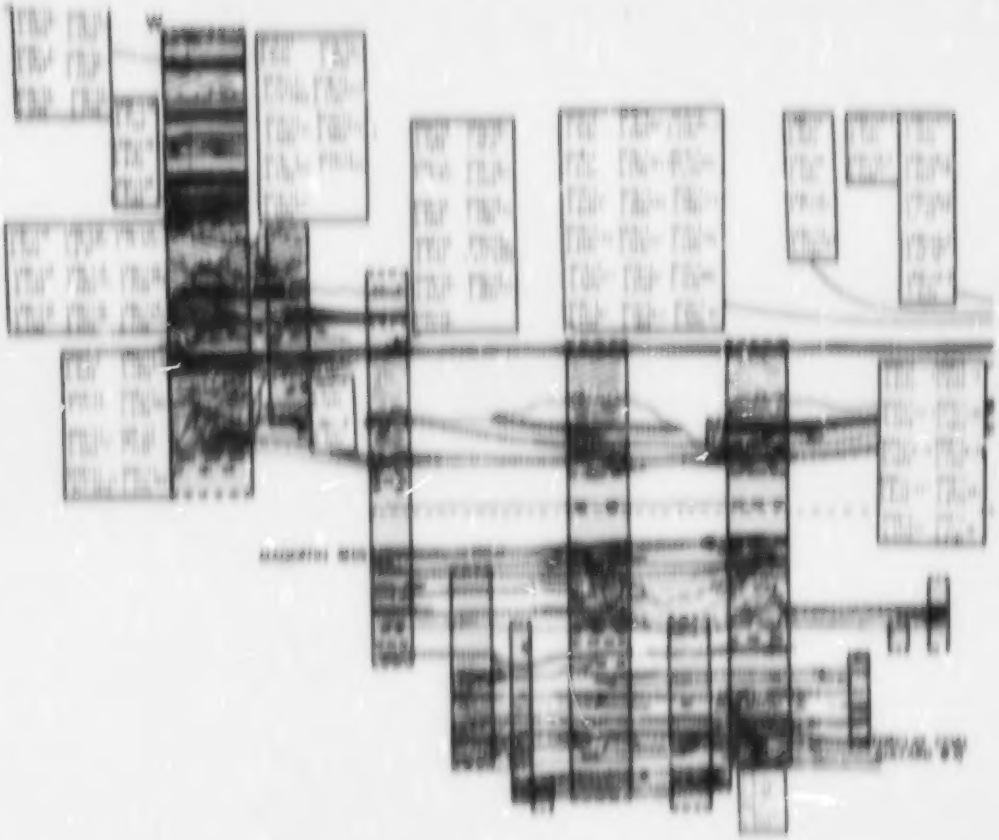


Figure 9a Geologic cross-section along Daniel Boone Parkway near Hazard, Kentucky (western half).

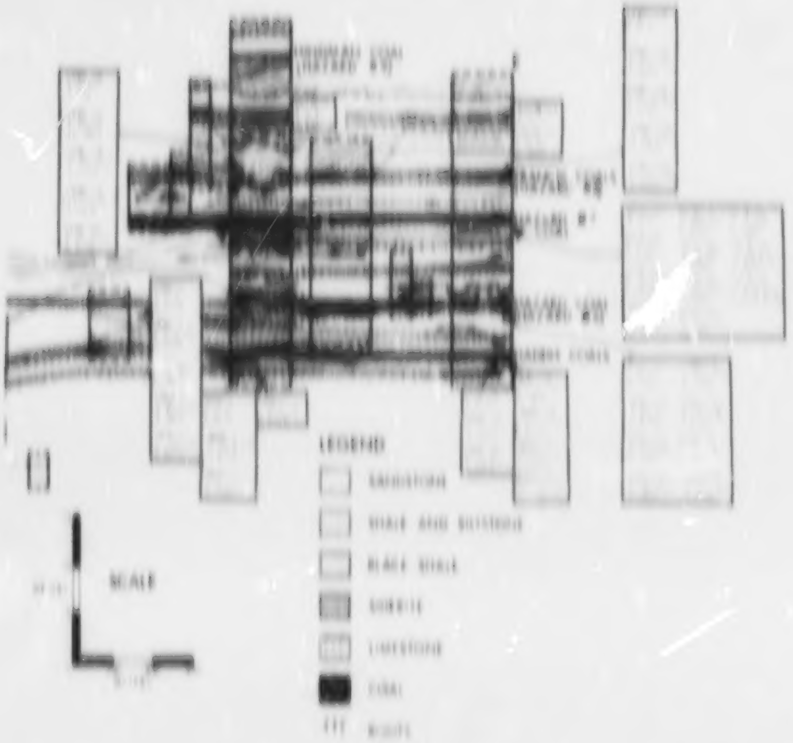

LEGEND
SANDSTONE
SHALE AND SILTSTONE
BLACK SHALE
SIDERITE
LIMESTONE
COAL
SCALE

Figure 9b. Geologic cross-section along Daniel Boone Parkway near Hazard, Kentucky (eastern half).

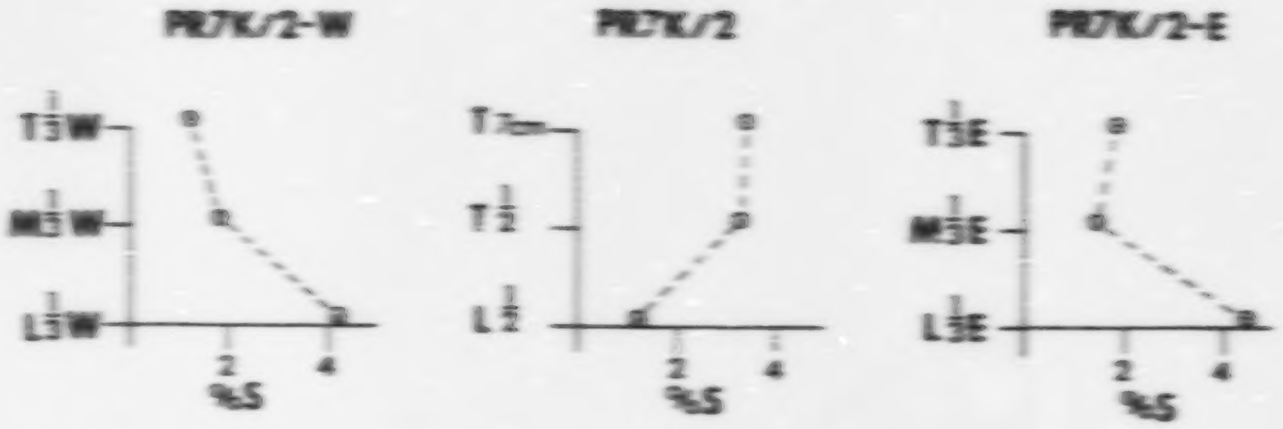


Figure III. Total sulfur contents of third-column samples of the Princess Seven coal collected one inch (2.54cm) apart.

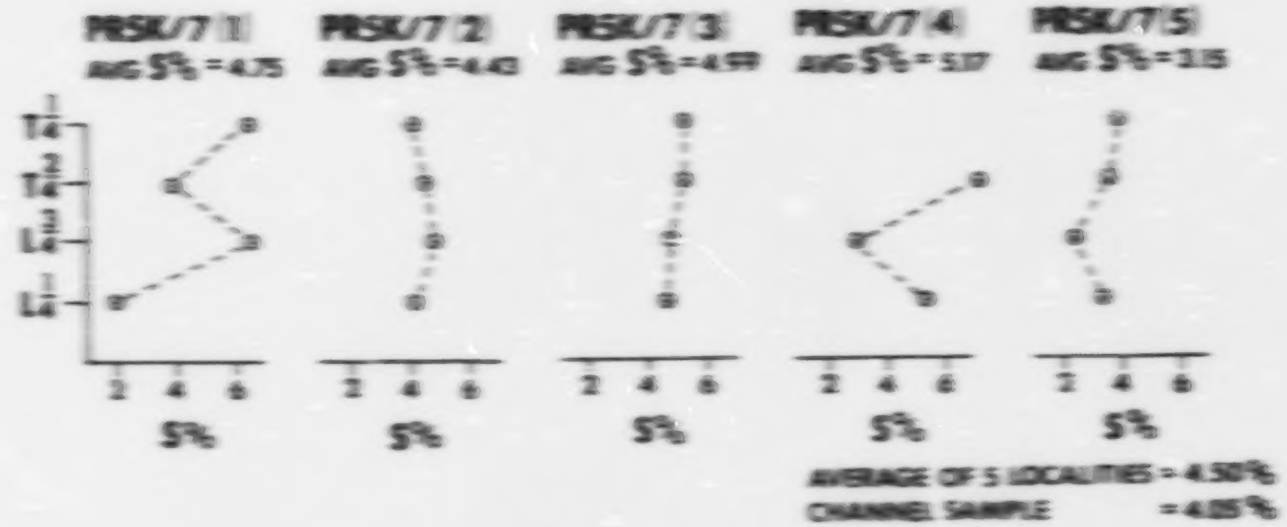


Figure 11. Total sulfur contents of quarter-column samples collected at PRSK/7.

## Variability Within a Split Coal Seam

Up to this point, the fact has been established that the total sulfur content within a coal seam has a tremendous variation in a vertical and horizontal spatial dimension of a coal seam of a uniform geology. To ascertain the variability of sulfur content within a split seam, an experiment was designed at station PR5K/1, where the Princess Five coal seam was observed to split into five different seams over a distance of approximately 100 feet (33 m). At this location channel samples of each split were collected and analyzed for total sulfur contents. The results of this study are summarized as follows:

| Location PR5K/1 | Split Sampled (Top to bottom) | Percentage Sulfur |
|---|---|---|
| | Top Split PR5K/1A | 7.70% |
| | PR5K/1B Split; Top-Half | 15.6% |
| | PR5K/1B Split; Bottom-Half | 4.5% |
| | PR5K/1C | 1.0% |
| | PR5K/1D | 1.2% |
| | Bottom Split PR5K/1E | 1.3% |

This detailed sampling plan further demonstrated that the sulfur content varied not only within uniform coal seams but within splitting coal seams as well.

## Laboratory Precision of Analyses

To test the precision of the laboratory analyses, the LECO Automatic Sulfur Titrator was used to analyze a series of coal samples whose total sulfur contents ranged from 0.5% to 5.5%. Selected samples having sulfur contents in the low and high range were chosen for replicate analysis and analyzed five to seven times. Within the low sulfur content coals (on the order of 0.6% sulfur), the analytical procedures had a variation of 0.03% sulfur. Analyses of samples with high sulfur content (on the order of 5.5% sulfur) had a variation of 0.1% sulfur.

These studies showed that the precision of the laboratory facilities was acceptable and that the sulfur variability within the coal was the dominant source of error. To reduce analytical error and to insure reproducibility, samples analyzed for total sulfur were staggered so that every other sample was analyzed twice. In addition, the LECO instrument was continually calibrated at the beginning of each analytical period to obtain a correct F factor for those sets of analyses. In this manner, trends in the analyses could be quickly ascertained and anonymous results readily identified.

## Limits of Interpretation

In summary, based on the above experimental designs, it was apparent that sampling problems existed because of the heterogeneous nature of the coal. One source of error occurs because the coal seams have a physical characteristic whereby degrees of friability are associated with low and high sulfur horizons. Coal seams usually are a mixture of blocky stratified horizons which are interbedded with laminated friable layers. The studies above showed the sulfur content to differ between the blocky and friable layers. In attempts to collect either column or channel samples of coal seams, the physical nature of the coal caused the blocky layers to be more abundantly sampled than the friable ones. It was noted, for example, that in channel sampling a coal, the blocky fragment commonly fell off the coal face in relatively large portions; whereas the laminated boney layers had to be chiseled away from the coal face to obtain equal portions. The former tended to contribute more to the sample, while the latter made up less of the total volume. As a result, the blocky layers within the coal tended to overshadow the laminated friable layers and accordingly dominated the sample analysis. However, in this study attempts were made and care taken to insure that equal volumes of coal were collected from each horizon.

In future studies, it is suggested that coal be sampled with the aid of a mechanical device that would withdraw uniform volumes of material throughout the entire seam. It would be possible, for example, to channel sample the entire seam with an auger or corer to prevent the physical segregation of the blocky material from the laminated material.

Within each coal seam, micro-environments are known to be interbedded throughout the seam. In this study, coal seams identified and chosen for sampling were at locations where the paleoenvironment of the overlying strata was overwhelmingly of one type. Areas of questionable or mixed paleoenvironments were not sampled. Even with these field precautions, it is readily apparent that micro-paleoenvironments exist within the seams and there is no known way of accurately identifying each micro-horizon within each coal. The variations in sulfur contents expressed above may be due to these uncertainties.

In this study, and guided by detailed field mapping, samples were colected from coals that were best identified as being representative of particular paleoenvironments. The following conclusions are drawn from data that were obtained within the limits of the mapping technique and are cognizant of the variations in sulfur contents that are known to exist within the coal seams. Until a sampling plan is designed that can adequately sample the heterogeneous nature of the coal and a technique devised to identify the micro-paleoenvironments in the coal seam, the conclusions of this study must necessarily be constrained within these limits.

## OCCURRENCE OF FRAMBOIDAL PYRITE

### Types of Pyrite

A variety of pyrite morphologies exists within a coal seam which can be related to either the early phase of the formation of coal (pyrite being deposited contemporaneously with the peat) or emplaced subsequent to the coalification of the peat (pyrite being mobilized and subsequently deposited within a solid coal seam as secondary pyrite). Gray, et al. (1963) described the morphologies and occurrence of the pyrite forms within the Pittsburgh coal seam and how they relate to the effectiveness of coal cleaning processes. In a study by the Ohio State University Research Foundation (1970), Stiles proposed a classification of pyritic material in coals within two main categories: primary pyrite and secondary pyrite. Within the primary pyrite category, sulfur balls, finely disseminated pyrite and primary replacement pyrite are included. The latter category includes secondary replacement and fracture filling pyrite. In the present study, pyrite morphologies have been grouped into five categories which are characterized as 1) primary massive, 2) plant replacement pyrite, 3) primary euhedral pyrite, 4) secondary cleat (joint) coats, and 5) framboidal pyrite. Each of these types of pyrites was noted to occur in the coal samples examined with an ore light reflecting microscope. Of the five categories mentioned, the framboidal pyrite is most reactive, readily oxidizes and is primarily responsible for the generation of acid mine drainage.

In the first two categories, the primary massive and plant replacement pyrite are commonly 150 to 600 microns in size. In most cases, the pyrite retains the cellular structure of the material that the pyrite emplaced and can be readily identified with a microscope. Examples of the primary massive, plant replacement pyrite are illustrated in Figures 12-15. In Figure 12, vessel walls (tracheids) have been replaced by pyrite and the morphology of the containing unit can be readily identified. Figure 13 shows a mass of fusinite (ancient charcoal) encapsulating massive coarse grained pyrite. Figures 14 and 15 illustrate how coarse grained pyrite has replaced existing cell structures within the coal. These primary pyrite features frequently occur within coals and do not appear to have been compressed. In contrast, the layers of coal adjacent to these pyrite replacement features appear compressed and compacted; whereas the pyritic features show no visible signs of compression. These relationships suggest that these massive pyrite particles were emplaced syngenetically with the deposition of peat and are considered as primary in origin; that is, forming at the time the peat is deposited.

A third category of pyrite includes primary euhedral pyrite, which, too, is noted to occur within coal seams and is surrounded by layers of coal that were compressed. These crystals, or euhedra, of pyrite are commonly shaped as either cubes or dipyramids and are 0.5 microns to 2 microns in size. Individual crystals may occur as discrete grains widely disseminated within a coal (Figure 16), clustering along layers (Figure 17), or within spherical agglomerations (Figure 18), which are collectively called framboidal pyrite.

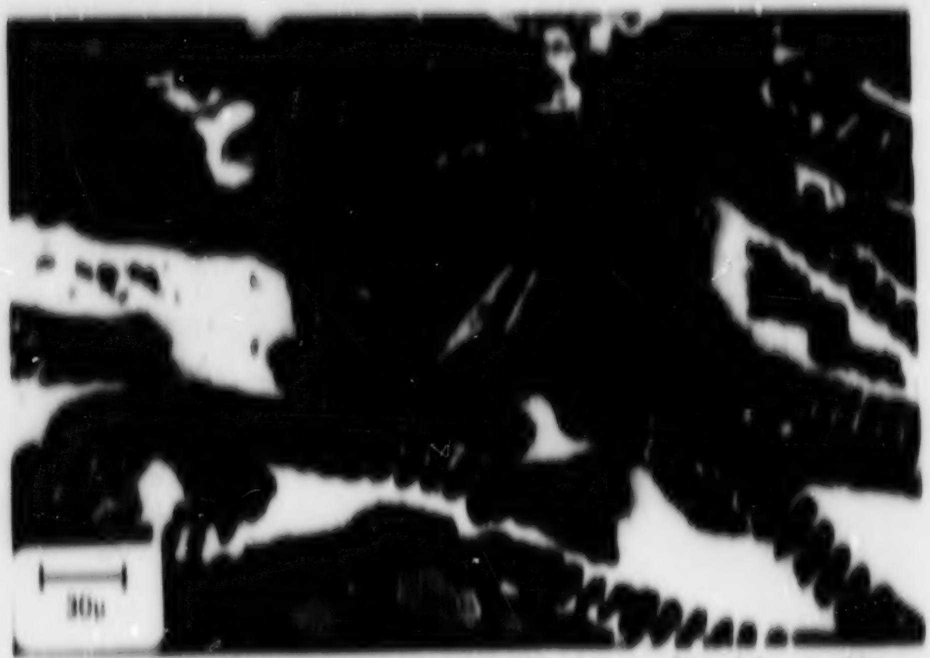


Figure 12. Photomicrograph of tracheids replaced by pyrite. (Sample PR7K/2-L 1/3)

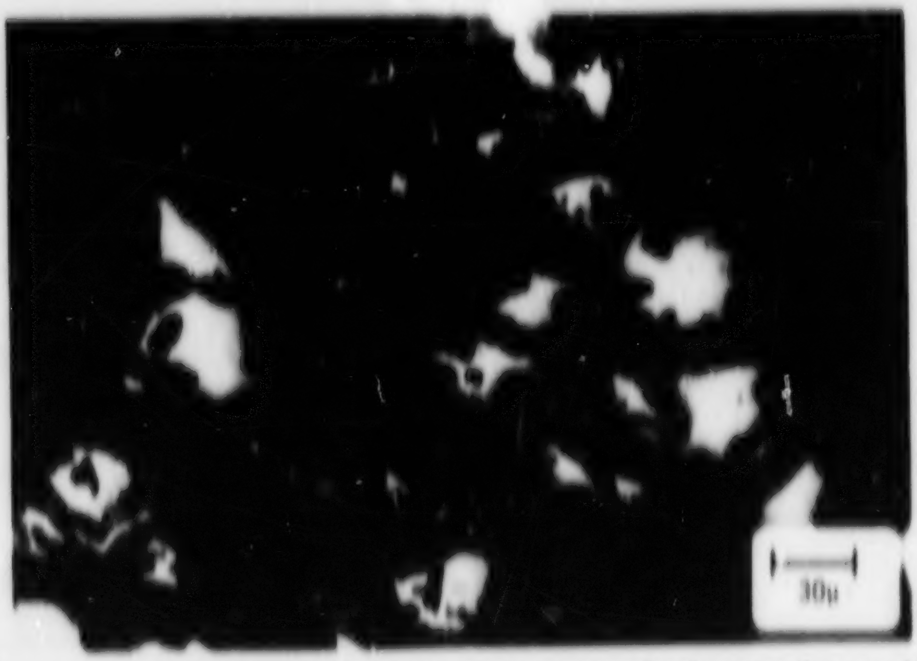


Figure 13. Photomicrograph of fusinite encapsulating massive pyrite. (Sample PR7K/2-L 1/2)

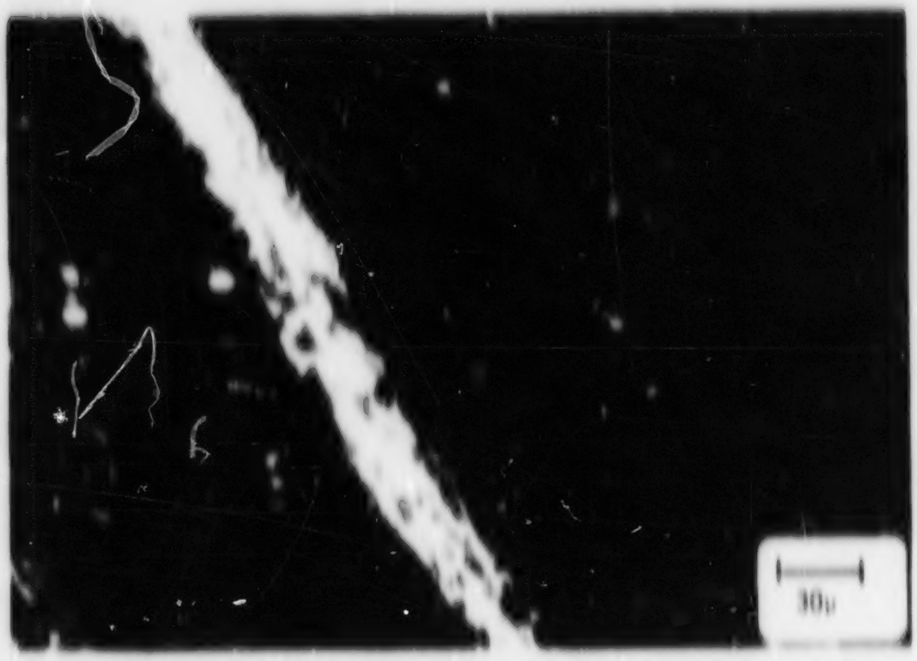


Figure 14. Photomicrograph of plant cells replaced by pyrite. (Sample TCK3/1-M 1/3)

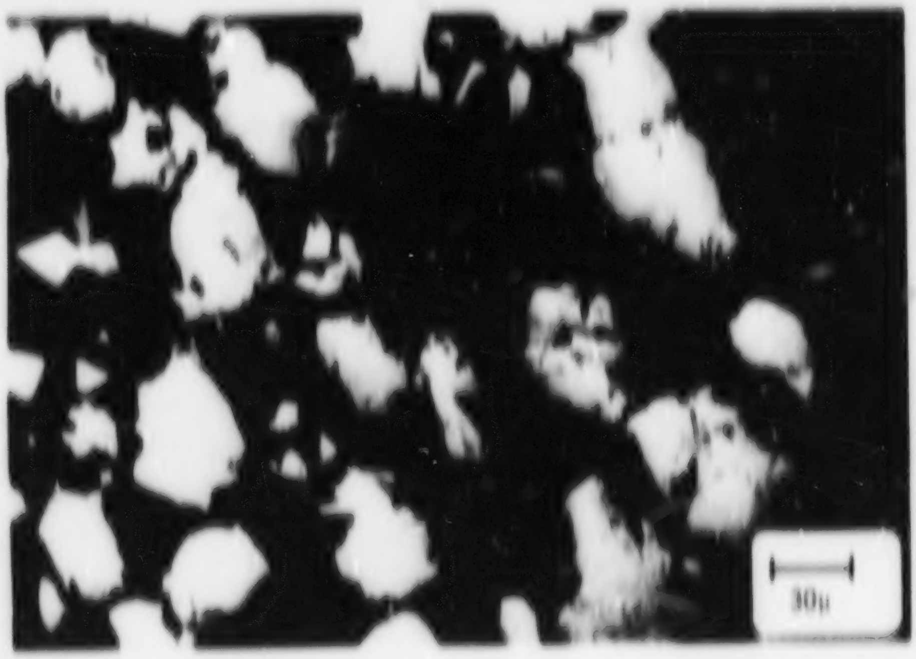


Figure 15. Photomicrograph of massive pyrite grains within plant material. (Sample TCK/4-L 11")

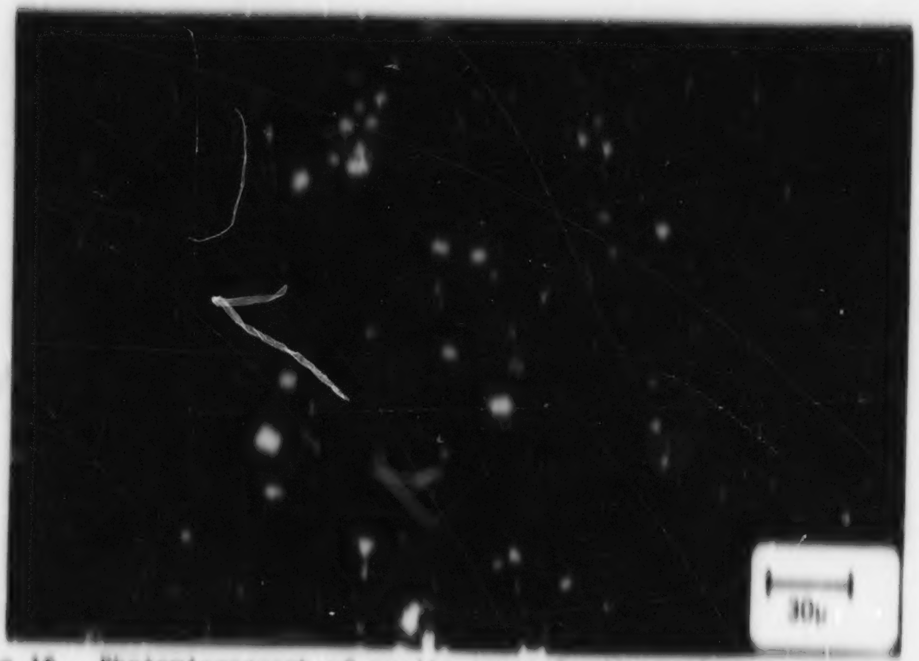


Figure 16. Photomicrograph of pyrite crystals disseminated within a coal. (Sample PR7K/2-M 1/3E)

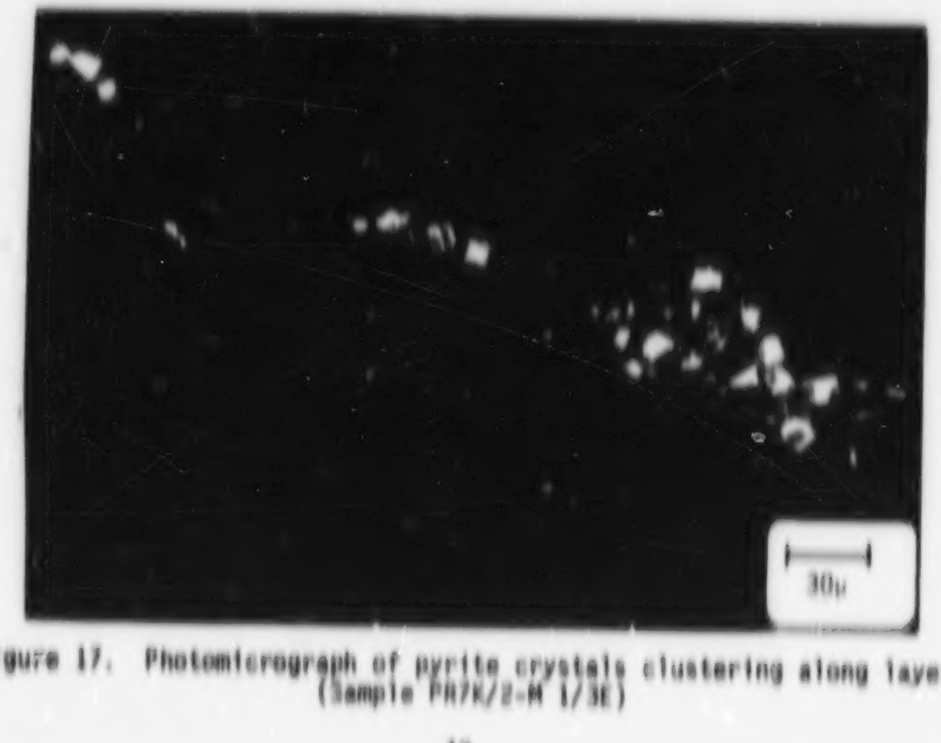


Figure 17. Photomicrograph of pyrite crystals clustering along layers. (Sample PR7K/2-M 1/3E)

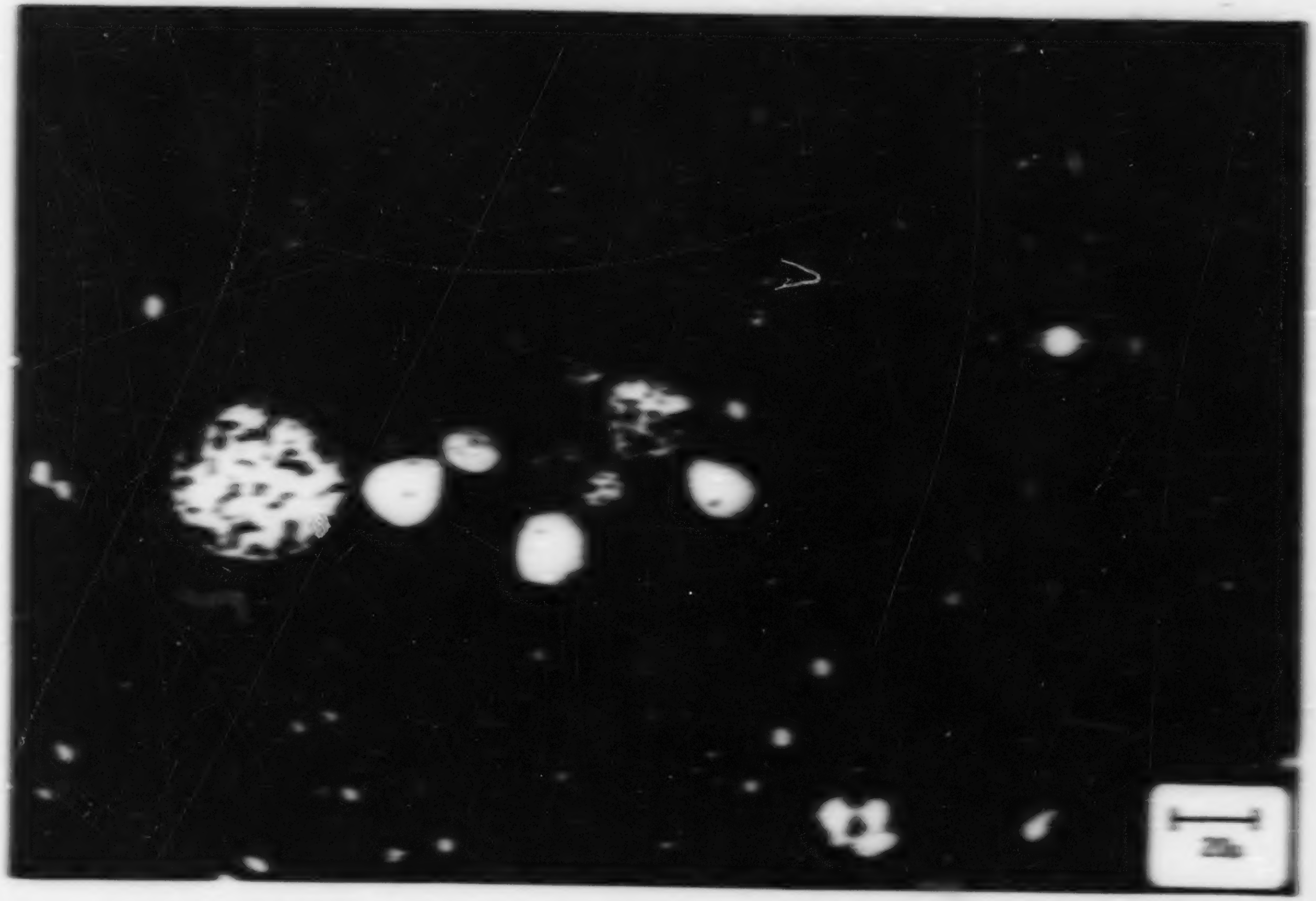


Figure 18. Photomicrograph of pyrite crystals within spherical agglomerations. (Sample below Hindman 9, Hazard, Kentucky area)

The microscopic examination of numerous polished pellets for this study showed euhedral crystals to occur both as disseminated particles and agglomerations forming the spheres of framboidal particles as well. In cases where the euhedral pyrite agglomerated and formed framboidal pyrite, the individual particle sizes never exceeded 1 to 2 microns.

The fourth type of pyrite classification used in this study includes the secondary cleat (fracture) coats. Figures 19 and 20 show how layers of pyrite coat the joints contained within the coal. It is readily apparent that this type of pyrite could not have been formed prior to the formation of joints within the coal and had to be mobilized and emplaced as a secondary feature subsequent to the coalification and diagenesis of the coal.

The fifth category of pyrite type used in this study, and the one that is most important, is the framboidal pyrite. The word "framboidal" comes from the French word meaning strawberries and describes the basic morphology that the framboidal pyrite has (Figure 21).

The origin and nature of framboidal pyrite has been the subject of many studies including those by Berner (1971), Richard (1970) and most recently, Javor and Mountjoy (1976). The similarities in morphologies that exist between the framboidal pyrite and microbial organisms have led some to suggest that framboidal pyrite has a microbial origin (Love, 1957; Love and Amstutz, 1966) and some to identify microbial species (Javor and Mountjoy, 1976). Most authors agree that framboidal pyrite formation takes place within the realm of a strongly reducing, iron rich, hydrogen sulfide emanating environment, whether it be in the skeletal remains containing cellular membranes or in an environment with an extraneous source of hydrogen sulfide that bubbles into the iron rich solutions. Whatever the mechanism, a distinct relationship exists between the occurrence of framboidal pyrite and strongly-reducing organic rich environments.

Some interesting data regarding the formation of framboidal pyrite emerged from a recent investigation into the failure of culturing crabs in shallow marine farms fabricated from abandoned rice fields in the marshlands of South Carolina. The rice patties in this area have been abandoned for approximately 30-50 years during which time the fresh water barrier was breached and salt water encroached upon the field. During this 30-year interval the abandoned rice patties remained idle and were subjected to alternating fresh water-salt water flushing which eventually caused a brackish environment. In the recent past, during the futile attempts to flush out the brackish water and reinstill a salt water environment, for the purpose of harvesting marine shellfish, a strongly acidic, high sulfate-high iron pool of water was formed. Investigations by Czyscinski (1975) showed that the substrate underlying the abandoned rice pattie contained large amounts of framboidal pyrite which apparently formed during the past 30 years. In the attempts to redevelop a marine environment, the inflowing oxygenated waters oxidized the pyrite, produced acid mine drainage and killed the marine organisms. Interestingly, this study showed that the formation of framboidal pyrite can occur in short periods of time.

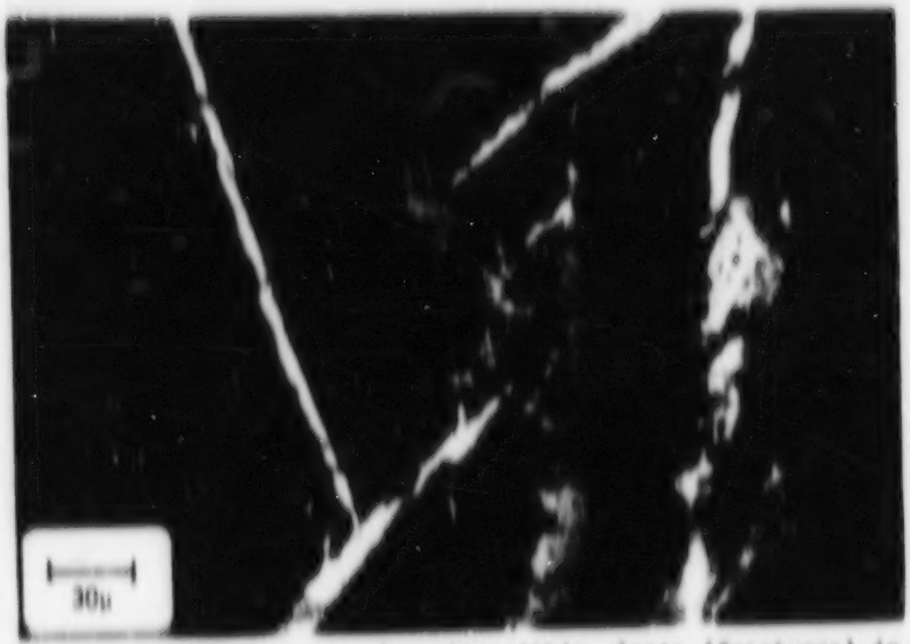


Figure 19. Photomicrograph of pyrite within cleats (fractures) in coal. (Sample PA/K/2-T 1/3W)

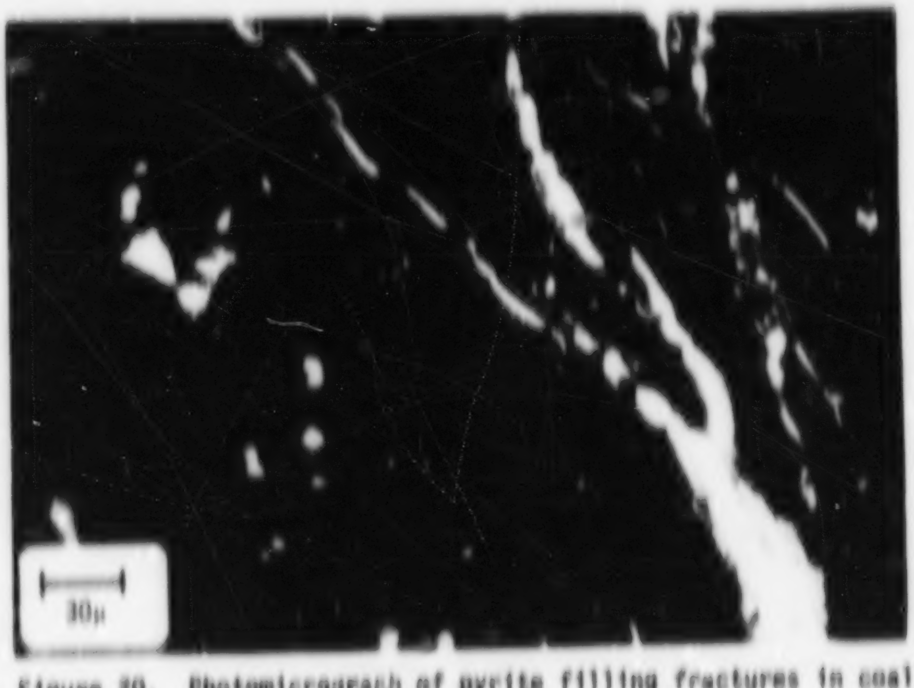


Figure 20. Photomicrograph of pyrite filling fractures in coal. (Sample TCK/9-CH)

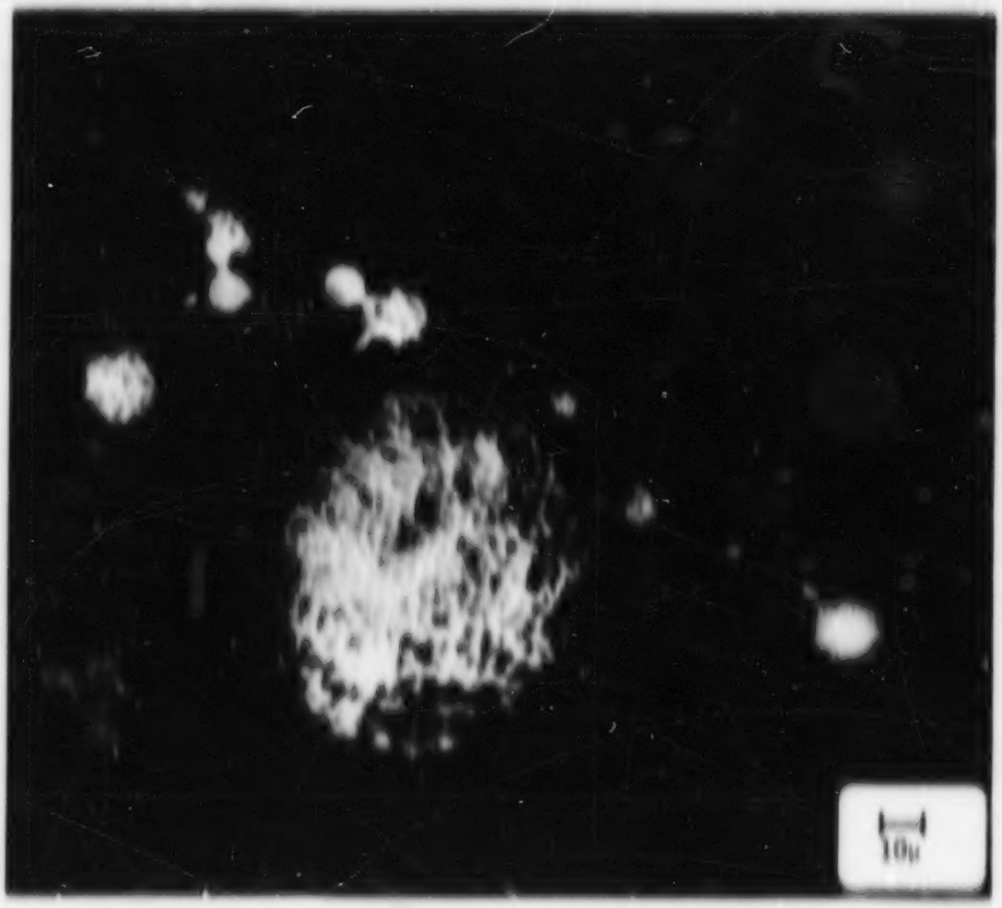


Figure 21. Photomicrograph of framboidal pyrite.
(Sample below Hindman 9, Hazard, Kentucky area)

Within the Carboniferous rocks, Caruccio (1968) showed that framboidal pyrite is the pyrite type that is the least stable and is primarily responsible for the production of acid mine drainage associated with coal mines. Framboidal pyrite can occur as spheres of crystals as illustrated in Figure 22, finely disseminated particles clustered along layers as in Figures 23A and 23B, or as scattered grains finely disseminated throughout the coal seam as shown in Figure 24.

One of the objectives of this study was to relate the occurrence of framboidal pyrite to coals of a particular paleoenvironment. The paleoenvironment was documented by the detailed mapping of the overlying strata, whereas the coal was the repository for the variety of pyrite types. In the course of examining numerous samples of coal seams from differing paleoenvironments for this study, each of the aforementioned types of pyrite was noted to occur throughout the sections. The nature of the coal simplified sample preparation and pyrite morphology identification. We readily acknowledge the fact that pyrite occurs throughout the strata of the geologic column as well as the coals. However, coals were used exclusively in this study because of their relatively higher sulfur contents which increased the pyritic sulfur content and facilitated the evaluation of the occurrence of framboidal pyrite.

## Method of Identification and Calculation of Percentages of Reactive Pyrite

Samples of coal collected and analyzed for total sulfur were subriffled into portions that were cast in epoxy pellets and finely polished for the microscopic examination of the various pyrite morphologies. Thus, the samples used in this phase of the study were split from and complement the samples used in the total sulfur analysis. Using these data, estimates of pyritic sulfur contents could be obtained and percentages of reactive pyrite could be ascertained.

The polished pellets were examined with an oil immersion light-reflecting ore microscope with a total magnification of 300X. Lower magnifications did not provide sufficient resolution to successfully identify the various morphologies. On the other hand, increasing the magnification beyond 300X led to a time consuming pellet scan as well as severe eye strain. For optimum viewing, with a large field for rapid scanning yet sufficient magnification for pyrite identification, it was found that 300X using a 10X ocular and 25X objective, coupled with a 1.2 internal magnifying index, gave the best possible results.

Each pellet was leveled onto a glass slide which was mounted in a stage micrometer. This permitted the sample to be scanned with overlapping parallel sweeps so that the entire surface of the pellet was observed. During these scans the area occupied by the various types of pyrite was noted and recorded. Upon completion of the scan of the entire pellet, the various percentages of the different types of pyrite were obtained to within 5% increments. These percentages of the various types of pyrite noted to occur in each coal seam and the percentage sulfur data of each sample are listed in Appendix A.

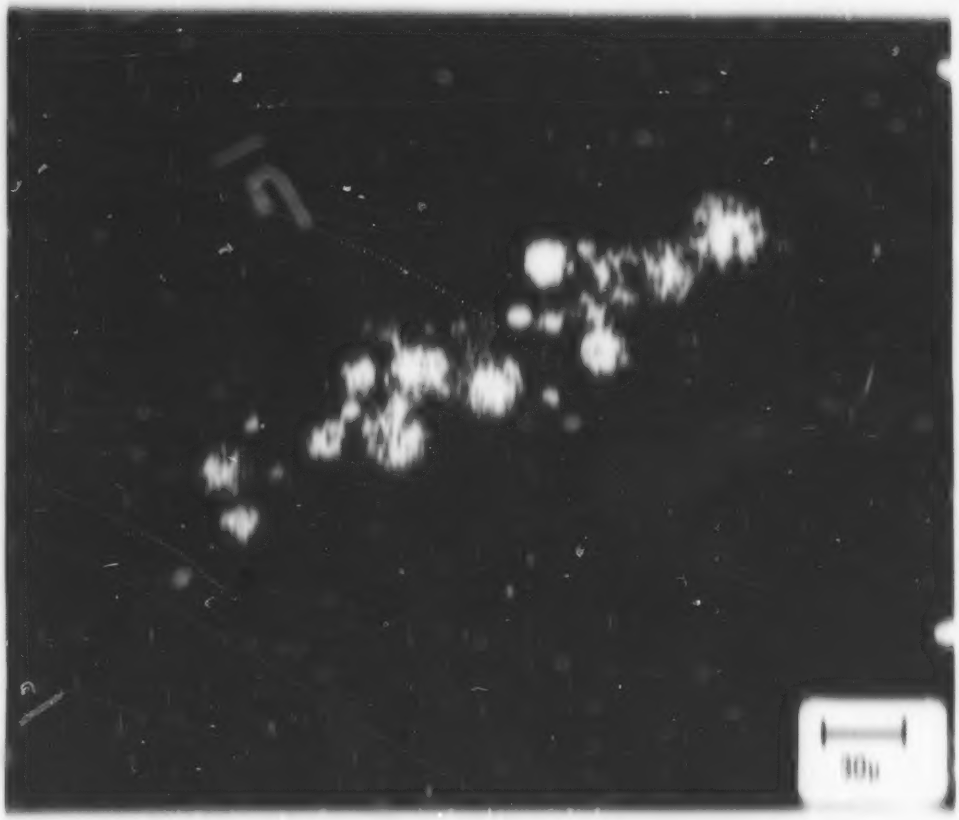


Figure 22. Photomicrograph of spheres of framboidal pyrite.
(Sample Hindman 9 coal, Hazard, Kentucky area)

Figure 23A. (300X)

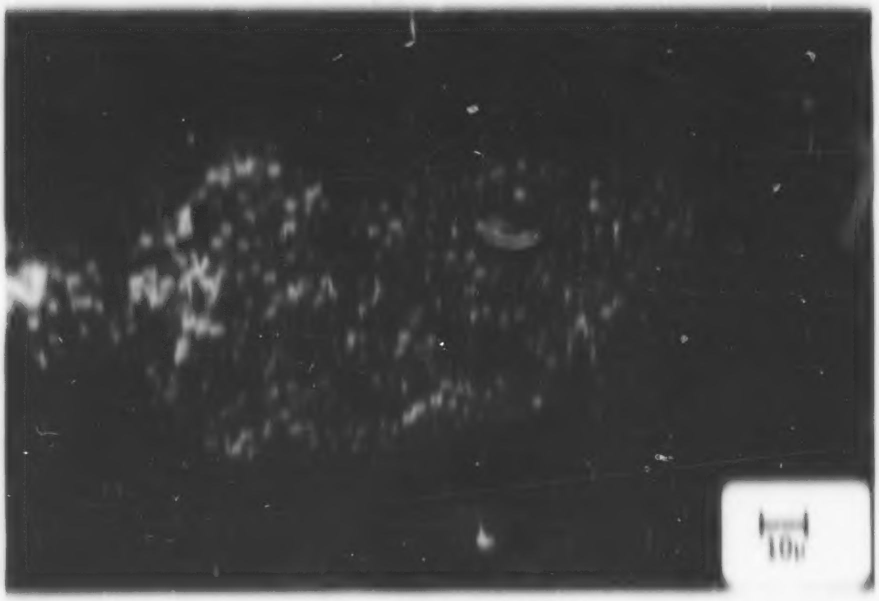


Figure 23B. (600X)

Figures 23A and 23B. Photomicrographs of clusters of framboidal pyrite along layers: A at 300X, B at 600X (sample TCK/2-L 1/2).

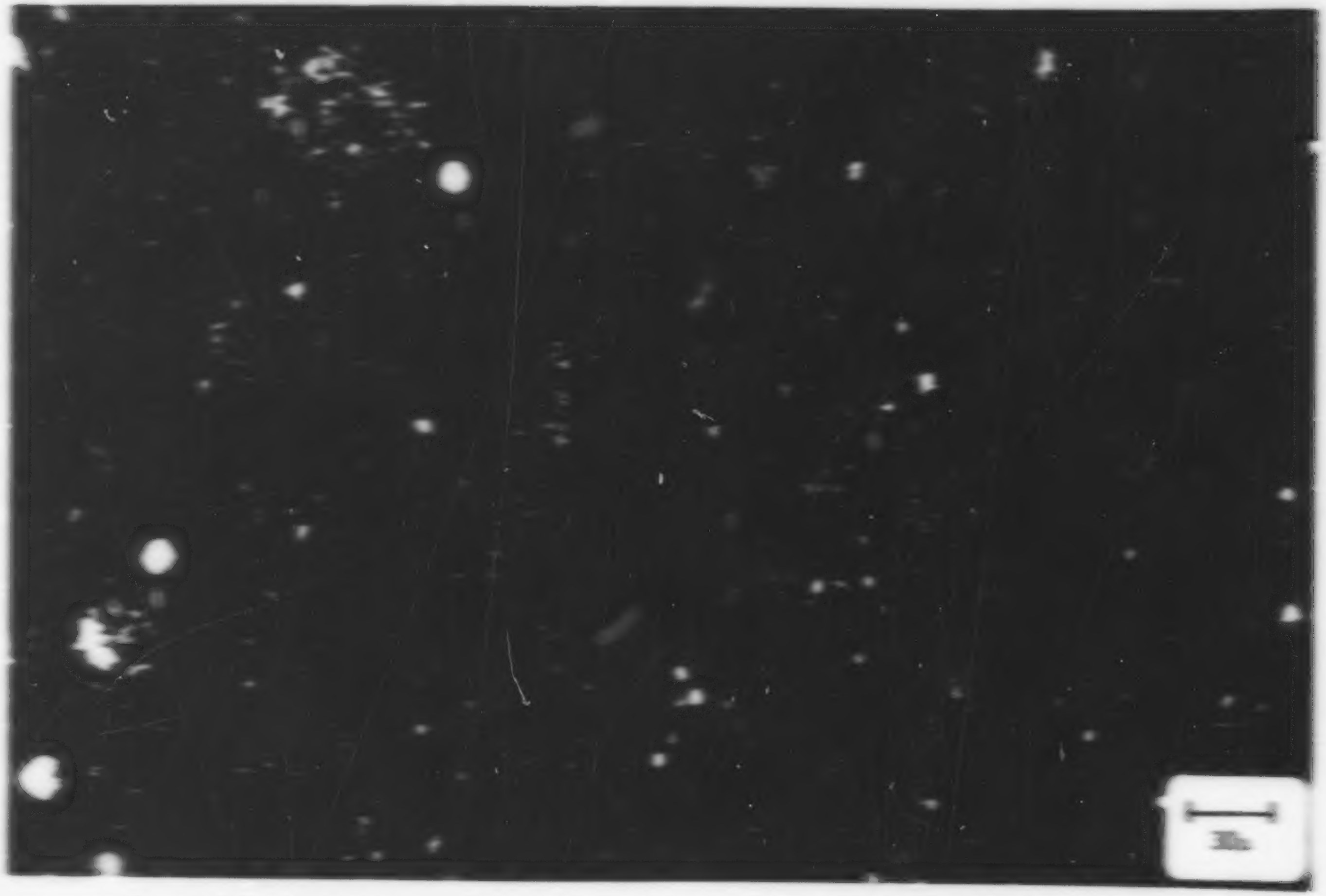


Figure 28. Photomicrograph of framboidal pyrite scattered throughout the coal.
[Sample PIT/2-L 1/30]

Given the premise that the framboidal pyrite is the most reactive of the pyrite types, coupled with the assumption that variations of total sulfur contents reflect variations in pyritic sulfur contents of the samples, the percentage of reactive pyrite occurring within each sample can be calculated.

An empirical relationship between total sulfur and pyritic sulfur was derived by Leighton and Tomlinson (1960, in Given, 1969) which can be used to obtain the pyritic sulfur content of the sample. The relationship is expressed by:

$$S_{pyritic} = 0.78\, S_{total} - 0.49 \qquad (8)$$

Using this equation, the total sulfur contents of the samples can be used to calculate the pyrite content of the samples.

Most of the samples collected for this study were column samples, and the sulfur analyses show the sulfur content of that particular interval of the seam. The intent of this study was to compare seams of various paleoenvironments and accordingly all of the sulfur data were weighted by the sample interval thickness to get an average sulfur content for the entire seam. These data appear in Appendix A-2.

The average sulfur content for the seams were then used in equation (8) to calculate the pyritic sulfur content of the seam (Appendix A-2).

Subsequently, the relative percentages of the various pyrite types were weighted by the sample interval thickness to obtain the average framboidal pyrite content of the whole seam. To obtain the absolute percentages of framboidal pyrite, the pyrite content of the seam was multiplied by the relative percentage of framboidal pyrite. This gave the percentage of framboidal pyrite occurring in the coal seam (Appendix A-2).

## Comparison of Framboidal Pyrite Contents of Coals of Various Paleoenvironments

In reviewing the data, it became readily apparent that the total and pyritic sulfur contents of samples collected from the Hazard, Kentucky area were markedly higher than those collected from the road cut sections along Kentucky Interstate 64 between Grayson and Ashland, Kentucky. This suggested that there were significant differences in the sulfur contents of samples from varying geographic areas. Thus, to make a valid comparison between coals of different paleoenvironments, the comparison must be made between coals collected in a common geographic location.

Based on those considerations, the samples common to the Hazard-Daniel Boone Parkway area of Kentucky were separated from those collected along the I-64 Grayson-Ashland sites. The framboidal and total pyrite percentages of each seam, as calculated and shown in Appendix A-2, are plotted for those samples from the Hazard area (Figure 25) and for those samples from the I-64 area (Figure 26). There is no importance to the order in which the individual samples are arranged along the vertical axis. In Figure 25 the Hazard Six and Haddix coals represent the upper delta plain sequence; the Hazard Seven and

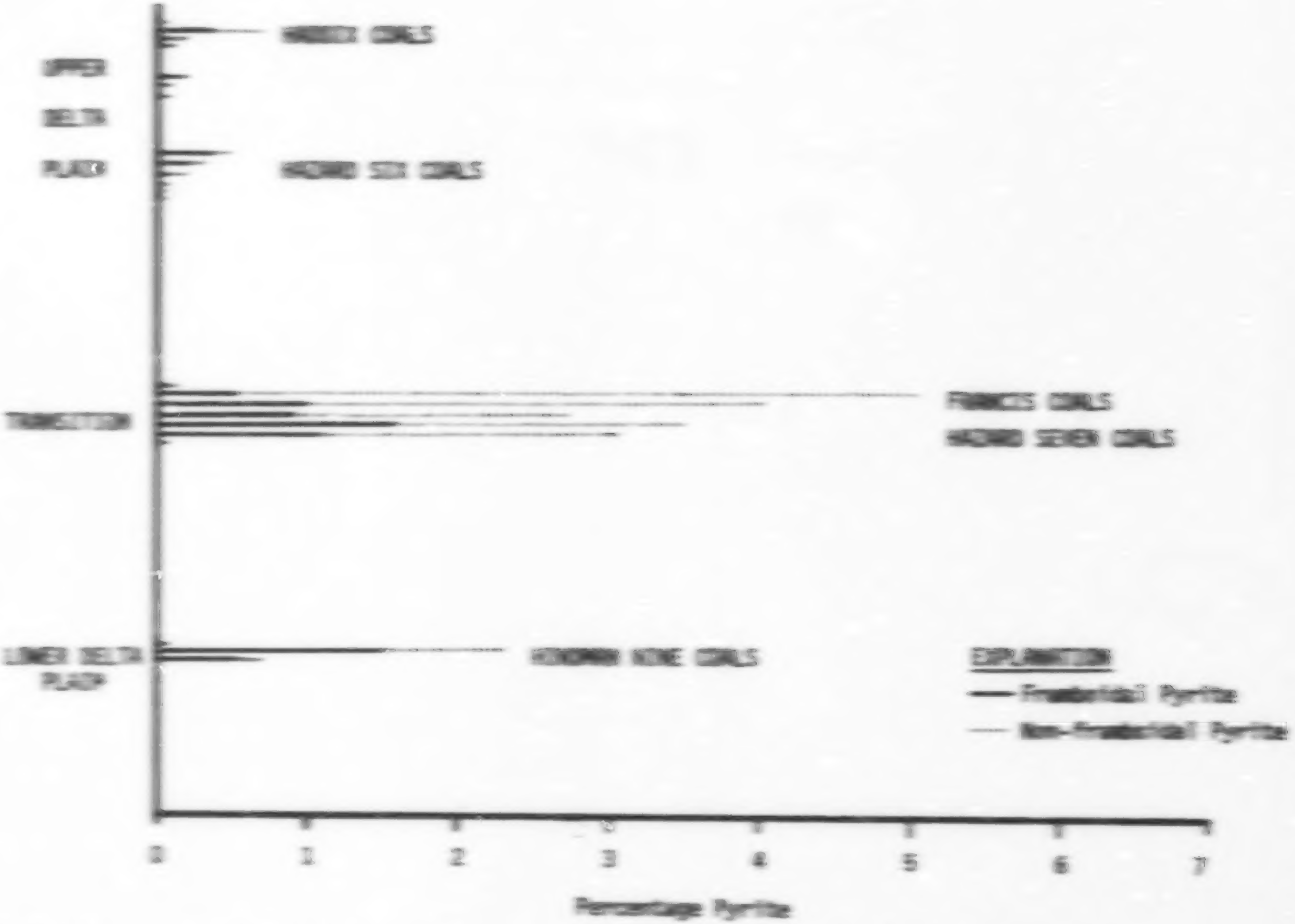


Figure 25. Distribution of framboidal pyrite and total pyrite for coals collected from the Hazard area and grouped into paleoenvironments.

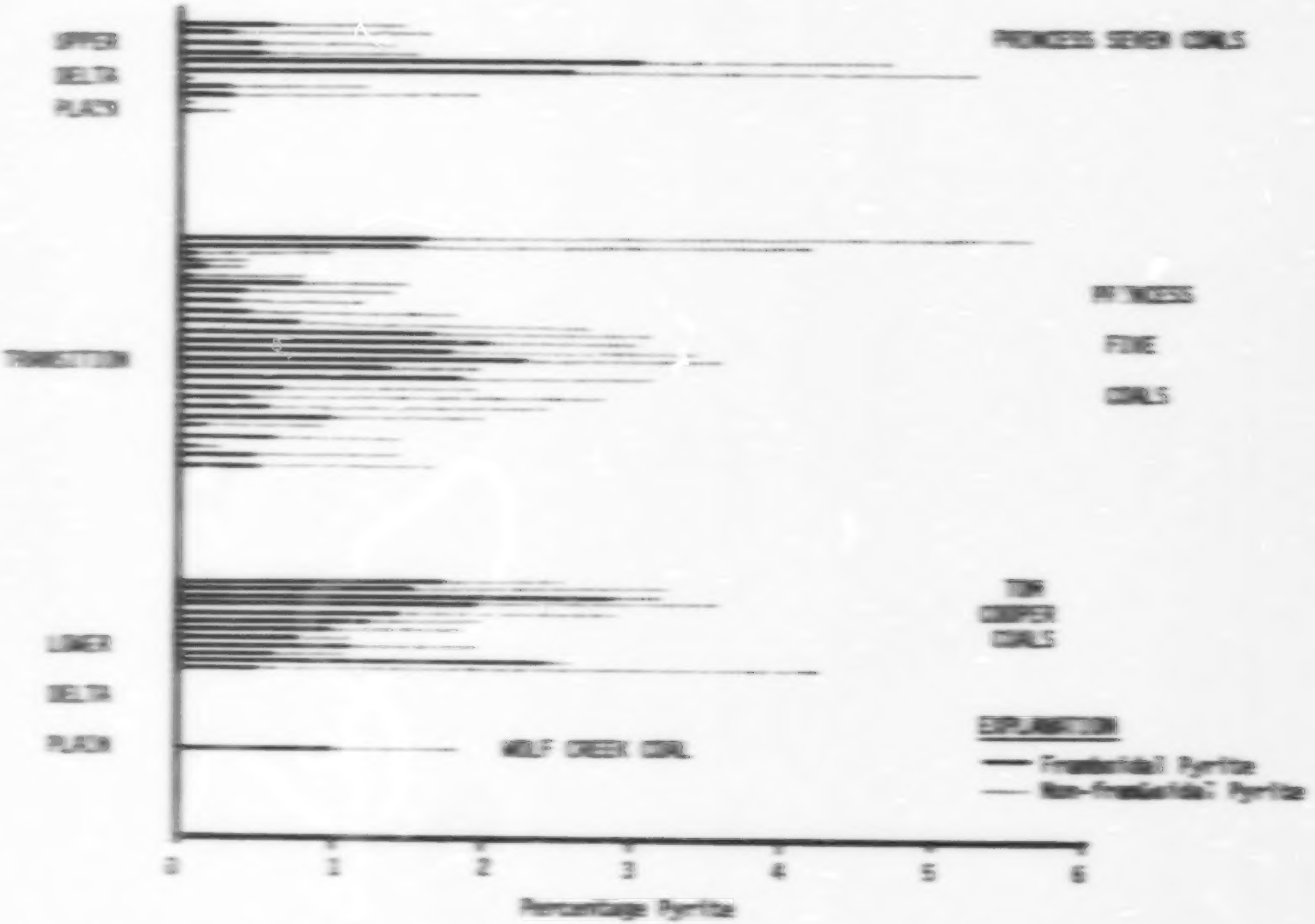


Figure 26. Distribution of framboidal pyrite and total pyrite for coals collected from the I-64 road cuts and grouped into paleoenvironments.

the Francis coals represent the transitional paleoenvironment, and the Hindman coals, the lower delta plain. In Figure 26, from top to bottom the Princess Seven coals represent the upper delta plain, the Princess Five coals the transitional, and thw Tom Cooper and Wolf Creek coals represent the lower delta plain paleoenvironment.

Comparing these two figures, it becomes readily apparent that a significant difference in total and framboidal pyrite content exists between coals of similar paleoenvironments collected from different geographic areas. The coals representative of a particular paleoenvironment collected from one geographic area were not the same as those from the other area. For example, in the Hazard area the Haddix and Hazard Six coals were representative of an upper delta plain environment, whereas in the I-64 areas the Princess Seven coals were chosen to be representative of a similar paleoenvironment. Thus, in order to compare coals of various paleoenvironments, the results obtained from the I-64 sites were used in preference to those of the Hazard area; a larger number of samples being a major consideration in choosing these data.

The histograms plotted in Figure 26 show that framboidal pyrite is found in coals of all paleoenvironments and is not restricted to the marine-transitional environments as had been supposed. However, it appears that framboidal pyrite is more prevalent in the marine-transitional facies than the upper delta plain facies.

This hypothesis was tested using a Chi Square test which showed that there was a significant difference in the percentage of framboidal pyrite in the upper delta plain coals when compared to the transitional lower delta plain coals (at the 90% level).

A one-way analysis of variance, coupled with Bartlett's test, showed that there was no significant difference when the upper delta plain coals and the lower delta plain coals were compared to the transitional ones, but that there was a significant difference (at the 95% level) when the upper delta plain coals were compared to the lower delta plain coals. Inasmuch as the transitional environment is a blend of the extreme environments, it is to be expected that the coals from all three environments would be similar when compared to the "median" environment. However, it is significant that the lower delta plain coals contain more framboidal pyrite than the upper delta plain coals.

In view of the variability of total sulfur content that occurs within coals, it becomes apparent that a similar variability also exists within the distribution of framboidal pyrite. Quite possibly these reflect variations of micro-paleoenvironments within one coal seam. In general, though, greater percentages of framboidal pyrite, combined with a greater percentage of pyritic sulfur, occur in lower delta plain sequences when compared to the upper delta plain-alluvial sequences.

Within the limits of interpretations constrained by the variability of the total sulfur contents that was previously noted, a positive relationship exists between the occurrence of framboidal pyrite in lower delta plain sequences and a relative paucity of framboidal pyrite in the upper delta plain sequences.

## LEACHING TESTS

The hypothesis outlined above basically relates the occurrence of framboidal pyrite to the depositional environment of the strata. In so doing, the occurrence of reactive pyrite can be approximated and predicted. Inasmuch as one of the major objectives of the study was to predict the occurrence of acid mine drainage, a study was designed to test a group of coal seams from varying paleo-depositional environments to ascertain the degree of acid production that could be expected from each coal. For this purpose, a series of leaching tests was designed to test the amount of acid each coal would produce.

### Sample Selection

Within the area of eastern Kentucky, five coals of varying paleoenvironments were identified and chosen for the leaching tests. The coal samples selected for the leaching study were collected from the Hazard area in eastern Kentucky and represent various depositional environments (Figure 27). The information pertinent to these samples is contained in Table 6.

TABLE 6. DESCRIPTION OF SAMPLES USED IN THE LEACHING STUDY

| Sample | Name of Seam | Paleoenvironment | Total Sulfur Content |
|---|---|---|---|
| A | Grassy #2 | Back barrier | 5.72% |
| B | Grassy #1 | Back barrier | 4.90% |
| C | Upper Whitesburg | Lower delta plain | 2.14% |
| D | Hazard #4, Top 12" | Upper delta plain | 0.61% |
| E | Hazard #4, Mid 12" | Upper delta plain | 0.61% |
| F | Fireclay | Lower delta plain | 0.61% |
| G | Fireclay | Lower delta plain | 0.53% |
| H | Fireclay | Transitional | 0.43% |

### Method of Study

The eight samples that were collected and which were representative of the various paleoenvironments were split from the channeled field samples, crushed, sieved to a uniform size (2-4 mm), weighed and placed in plastic chambers which were continuously flushed with humidified air. At selected intervals, two to three times a week, the samples were covered with deionized water and drained. The volume of the effluent was measured and recorded and hot acidity determinations were made on an aliquot of leachate. Acidity values thus obtained could be converted readily to milligrams of acidity

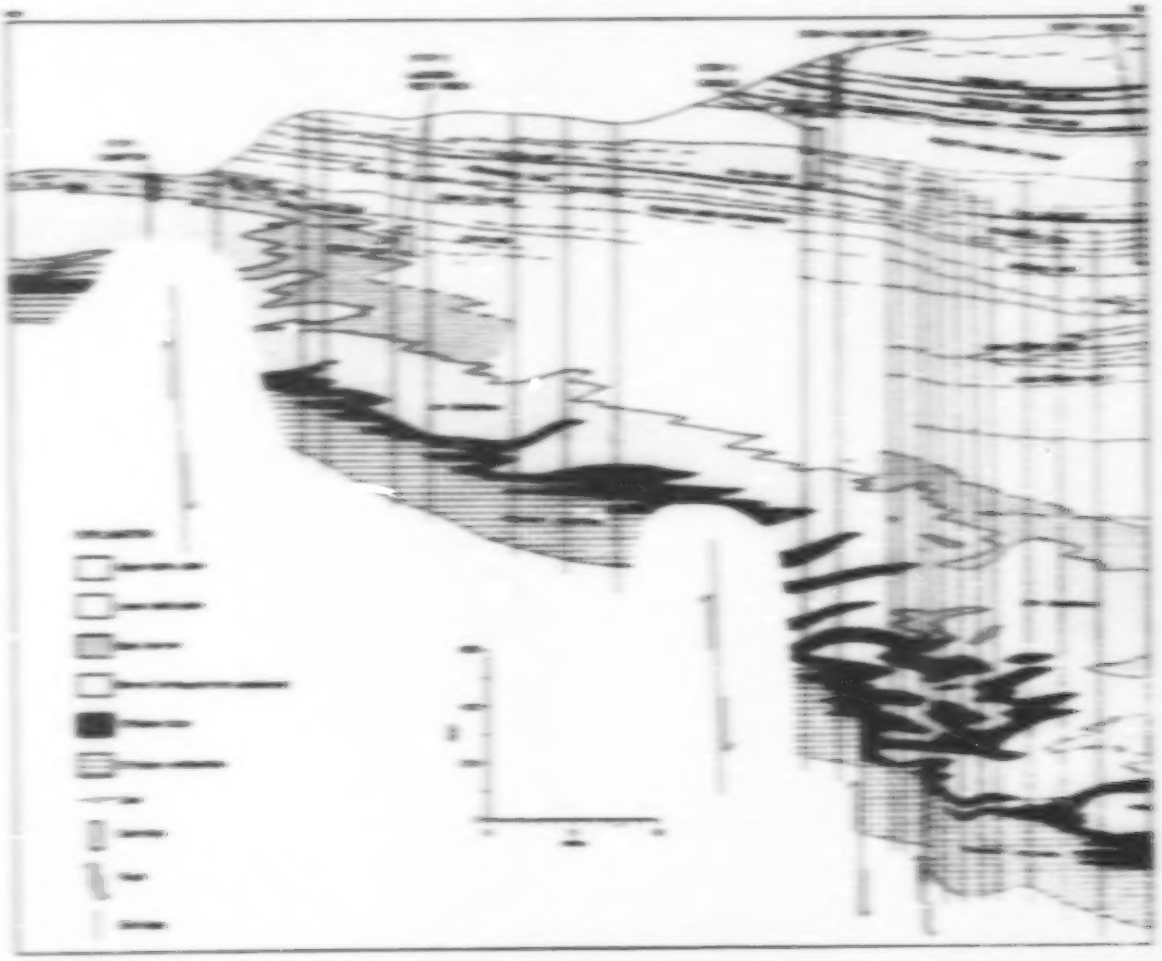


Figure 27. Geologic cross-section of carboniferous rocks between Pine Ridge and Vicco, Kentucky showing locations of samples used in the leaching study.

produced per volume of leachate. In turn, the amount of acidity could be adjusted to a common base and expressed as milligrams of acidity produced per 100 grams of sample. Cumulative acidity generated for each sample over a particular time period was then calculated and cumulative acidities graphically plotted to depict rates of acid production for each sample.

Results

Figure 28 shows the results of the leaching tests over a 25 day time period. The coal samples that were collected from the back barrier paleoenvironments produced more acid than the samples collected from the other depositional environments. Samples collected from the upper delta plain had low sulfur contents and did not produce appreciable amounts of acidity.

The leachates produced in this study were also analyzed for sulfate. The degree of sulfate present would reflect oxidized pyrite and approximate the percentage of reactive pyrite (framboidal) contained in the sample. On an average, the sulfate concentrations for the back barrier samples, samples A and B, were 1200 mg/l and 1300 mg/l, respectively. For sample C (lower delta plain), the sulfate concentration was 25 mg/l, while the remaining samples, which did contain small percentages of pyritic sulfur, had negligible amounts. On the assumption that sulfate anion is produced primarily from the decomposition of iron disulfide, it could be stated that samples A and B contain reactive pyrite, sample C contains minor amounts of reactive pyrite, while all others contain pyrite in a stable form which is not readily decomposing.

The results of the leaching tests, however, have limited application. The samples chosen for the study were selected to represent various paleoenvironments and it was hoped that the acid production potential of coal could be related to the paleoenvironment. The leaching tests did show that greater acidity was produced by the back barrier coals than by the upper delta plain coals, but this relationship can also be explained by the fact that the former have more total pyrite than the latter.

Another possibility exists that back barrier coals have higher sulfur contents than upper delta plain coals and consequently produce more acid. But as the sulfur variability studies showed, total sulfur contents and, for that matter, framboidal pyrite contents, vary across paleoenvironments, and only in general terms can it be stated that the back barrier samples are more sulfurous than upper delta plain coals. The probability exists that the back barrier samples used in the leaching tests were collected from high sulfur seams with gradations in between. Thus, in the leaching tests, the association of acid production with back barrier coals and lack of it with upper delta plain coals may be an artifact of sampling and not truly representative of acid production potential of various paleoenvironments. Inasmuch as these samples represent a small part of the total outcrop, it is quite probable, and in view of the variability in coal quality that can be expected, that an inadequate sampling program led to the fortuitous selection of upper delta plain coal samples which were exceptionally low in sulfur.

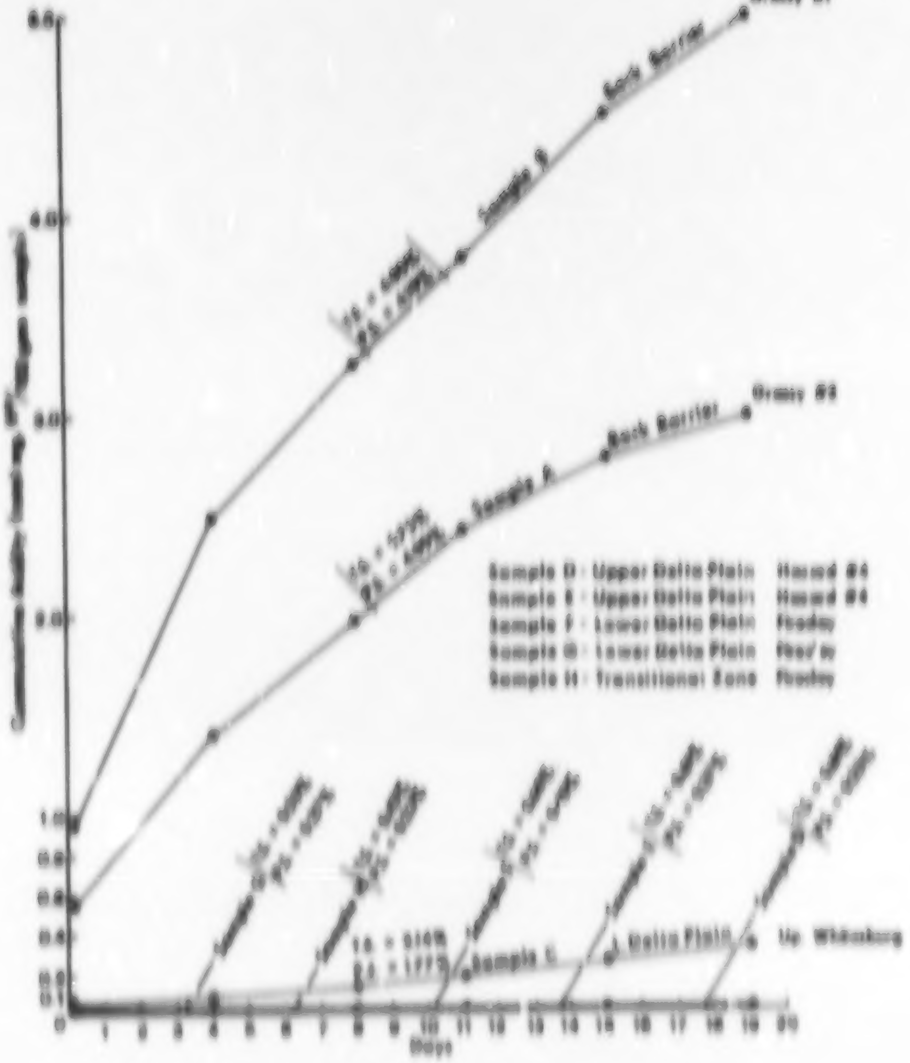


Figure 28. Plot of cumulative acidities per 100 grams of samples of varying paleoenvironments.

In this study, however, a strong correlation was shown to exist between the occurrence of reactive pyrite in the sample and sulfate anion in the leachate. This relationship plays an extremely important role in interpreting the aqueous geochemical data which will be discussed further in the following sections.

## AQUEOUS GEOCHEMISTRY

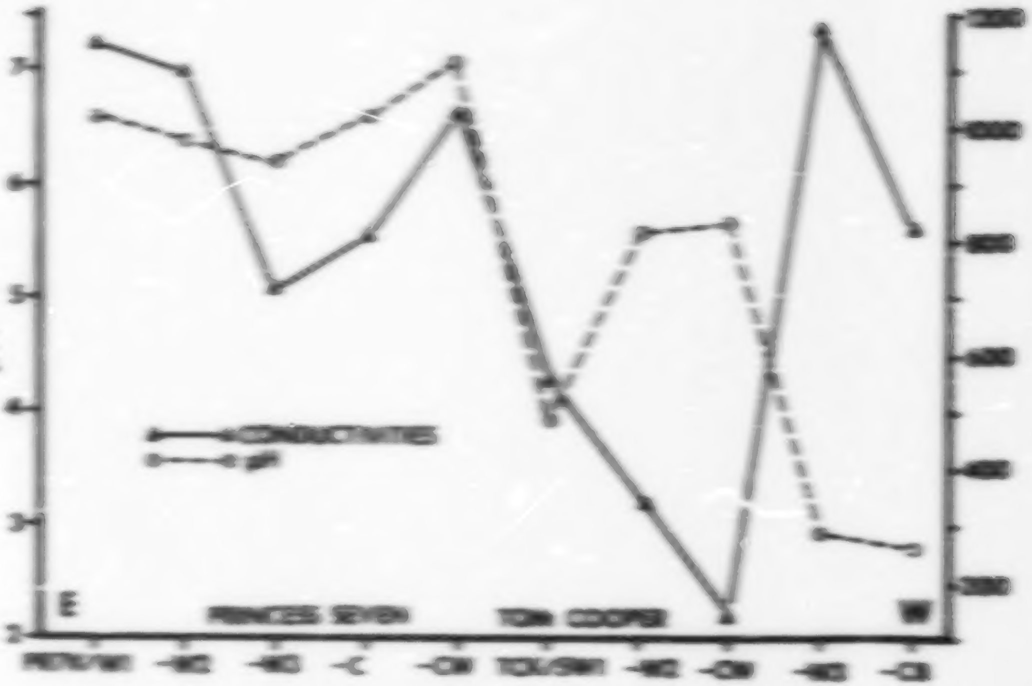
The ultimate quality of a mine drainage will be a combination of complex geochemical interactions of different ions from a variety of sources. It has been shown that the source of acidity, iron and sulfate in mine drainage is readily related to the occurrence and decomposition of framboidal pyrite. On the other hand, calcareous material found within a hydrogeologic environment presents the geochemical system with a natural buffering capacity. Ground water flowing within a geologic section, and contacting either or both of these geochemical effects, will pick up specific chemical species that reflect either of these reactions or combinations thereof.

This section discusses the importance of considering the ground water chemistry in predicting the quality of mine drainage that might be produced from a stratigraphic section. It has been shown that reactive framboidal pyrite occurs across strata of varying paleoenvironments, albeit in greater preponderance within coals associated with strata of lower delta plain-back barrier paleoenvironments. The leaching tests further showed that coals of a particular paleoenvironment were not only higher in sulfur but produced acid mine drainage as well. Both of these considerations neglect the natural aqueous geochemistry which will have a profound effect on the ultimate quality of mine drainage that is produced. The importance of considering the buffering effects of the natural system was best exemplified by a study by Biesecker and George (1966) who showed that streams degraded by acid mine drainage were ameliorated as they flowed into a more calcareous terrain.

### pH and Conductivity Trends Across Varying Paleoenvironments

Along Kentucky Interstate I-64 from Ashland to Olive Hill, a transition of paleoenvironments exists from an upper delta plain in the east to a lower delta plain to the west, where near Olive Hill the stratigraphy becomes more calcareous. Along this transition of paleoenvironments from Ashland to Olive Hill, a series of water seeps, small springs and streams adjacent to the highway occur and drain each of the various paleoenvironments. Along this profile, numerous opportunities exist to sample across paleoenvironments to compare water quality characteristics.

In a preliminary study, water samples were collected from seeps emanating from the Princess Seven and the Tom Cooper coal seams which are representative of strata of upper delta plain and lower delta plain, respectively, and analyzed for field pH and specific conductance. These data are plotted in Figure 29. In general, the water samples collected from the upper delta plain sequence have higher pH and conductivity values than samples collected from the lower delta plain sequence. These data reflect the occurrence of



CONDUCTIVITIES AND pH OF WATER SAMPLES
COLLECTED ALONG I-64, EASTERN KY.

Figure 25. Conductivities and pH of water samples collected along I-64, eastern Kentucky.

calcareous material in the upper delta plain strata which affords this water regime with a natural buffering capacity. This is further substantiated by the higher conductivities of water samples collected from this area. The pH's and conductivities of samples collected along the lower delta plain sequence are significantly lower than those found in the upper delta plain sequence, and the field data illustrate a gradual decline in these geochemical parameters in transgressing from one sequence to another.

The results of this preliminary study encouraged a more detailed regional investigation. Subsequently, water samples were collected from stations where the coal samples used in this study were previously gathered to relate water quality characteristics to the existing data. The following summarizes the results of the regional survey of the water quality analyses.

## Regional Water Quality Characteristics

All locations from whence coal samples were collected were revisited during the month of June 1975. At most of the locations, water samples were collected and analyzed for field pH, conductivity, acidity, hardness, and sulfate concentrations. The results of these analyses are summarized in Appendix B. In the following discussion, the sulfate, acidity, conductivity and pH values of water samples collected from the lower delta plain will be contrasted with those collected from the upper delta plain.

A perusal of the data in Appendix B shows that the pH of water samples from strata of lower delta plain paleoenvironments have low pH's which reflect lack of a natural buffering capacity within the section. In contrast, the pH of the upper delta plain samples show neutral and slightly alkaline trends. These trends basically corroborate the trends established from the preliminary survey along Interstate 64.

The conductivity data from Appendix B are grouped by various paleoenvironments and plotted in Figure 30. The acid mine drainages that were sampled during the survey are plotted at the top of the diagram for comparison. Interestingly, higher conductivities are noted for water samples collected from the upper delta plain sequence than those emanating from the lower delta plain sequence. This water quality trend, high conductivity and high pH, again suggests the presence of calcareous material. Obviously, alkalinity measurements would have more directly substantiated this premise, but because of the sampling difficulty and the inability to run alkalinity analyses within twelve hours (thereby precluding valid results), these analyses were not performed.

The sulfate values of the water samples shown in Appendix B were similarly plotted, grouping samples into lower delta plain and upper delta plain categories. In Figure 31, sulfate concentrations are plotted versus the paleoenvironment of the seam from which the water sample was collected. The values of acid drainages collected from the area are included for reference. Again, another interesting trend is observed. Sulfate produced primarily by the decomposition of the sulfide is readily abundant in water samples collected from the upper delta plain sequence. Because there are almost three times

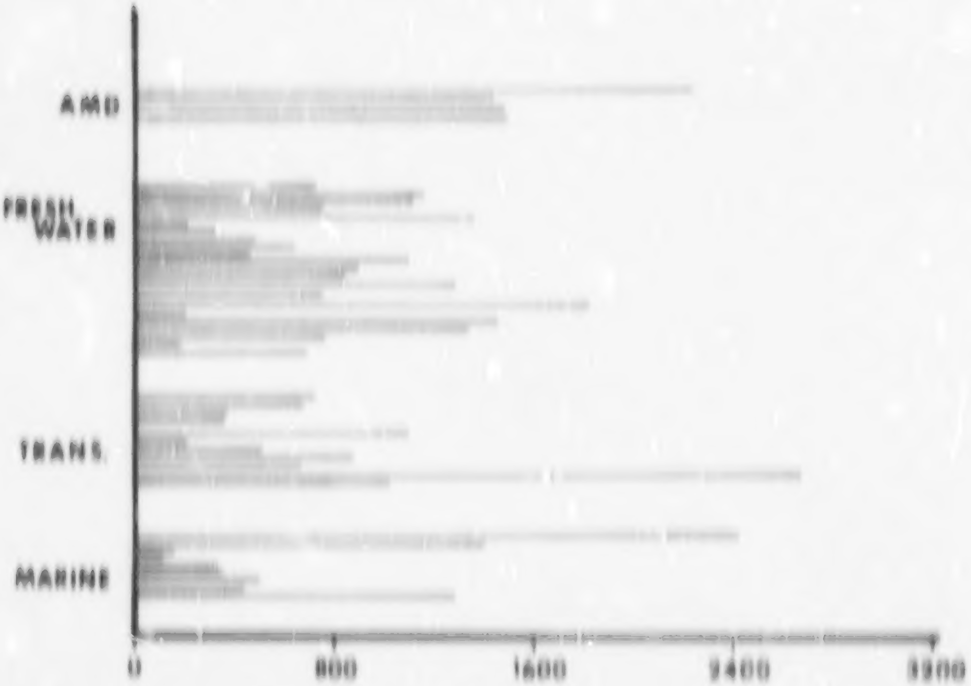


Figure 30. Conductivities of water samples from various paleoenvironments. (units are in umhos/cm)

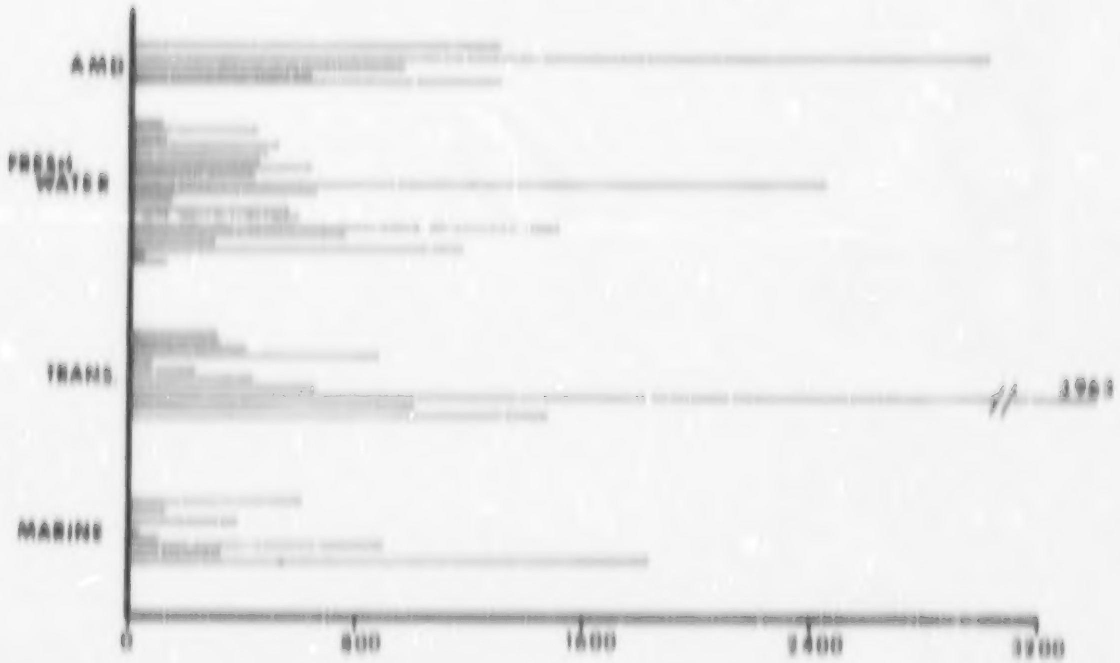


Figure 31. Sulfate content (mg/l) of water samples from various paleoenvironments.

as many samples collected from the upper delta plain sequence as there are from the lower delta plain sequence, a sample bias may be introduced which may affect the interpretations. The fact remains, however, that significant amounts of sulfate are found in water samples emanating from the upper delta plain rocks. This fact readily substantiates the data presented in Figures 25 and 26, which showed significant percentages of reactive pyrite to occur within coals from the upper delta plain paleoenvironments. The quality of ground water emanating from these coals further suggests that framboidal pyrite is present on a regional scale, as indicated by the significantly high sulfate concentrations of the water samples collected. Equivalent amounts of sulfate are also noted to occur in samples collected from the transitional and lower delta plain strata, which again substantiate the data derived from the microscopic examination of the pellets.

The analyses of water samples gathered on the regional basis represented to a greater degree the chemical composition and sulfur distribution within the coal seam. These water quality data, coupled with the data obtained from the microscopic examination of coal samples, substantiate the conclusion that framboidal pyrite is present in upper delta plain strata but not to the degree as noted to occur in the lower delta plain sequence. The fact that no acid is associated with the occurrence of framboidal pyrite in the calcareous rich strata underscores the importance of considering the ground water chemistry in attempts to ascertain drainage quality characteristics.

## CONCLUSIONS

1. In view of the variability of the total sulfur contents that was demonstrated to occur within uniform and geologically varying coal seams, any interpretations of the data, and conclusions derived therefrom, must be cognizant of this variability. The distribution of framboidal pyrite, as ascertained by the microscopic examination of the polished pellets, has been shown to be relatively abundant in seams of the lower delta plain paleoenvironments and also present in significant concentrations in coals of upper delta plain sequences. Statistical testing of regional trends, and within the limits of variation that can be expected to occur naturally, show that framboidal pyrite can be expected to be most prevalent in lower delta plain coals.

2. The leaching tests, which attempted to relate the occurrence of acid mine drainage to coals of varying paleoenvironments, were quite possibly influenced by the inherent natural variability. Fortuitously, the samples of upper delta plain coals had lower sulfur contents than those of the lower delta plain. Consequently, the strong correlation between acid mine drainage production and back barrier-lower delta plain coals and lack of acidity with upper delta plain coals may be an artifact of high and low sulfur coals and not related to paleoenvironment. The production of acidity from coals of a lower delta plain environment, however, can be correlated with the presence of framboidal pyrite as determined by the microscopic examination of the polished pellets. The lack of acid mine drainage from coals of upper delta plain used in the leaching tests may be due to the use of low sulfur coals with a paucity of framboidal pyrite. However, the leaching tests did show that sulfate anion concentrations can be used to identify the absence or

presence of weathered pyrite.

3. On a regional basis, a significant amount of sulfate was present in water samples collected from the upper delta plain paleoenvironment as well as those collected from the transitional and lower delta plain strata. The presence of sulfate anion is correlative with the occurrence of reactive pyrite, which substantiates the results of the reflected light microscopy.

4. The presence of sulfate in water samples collected from the upper delta plain sequence showed framboidal pyrite to be present in the Princess Seven, the Hazard Six and the Fireclay coal seams. Yet, in the majority of cases, these drainages were not acid, although they had high specific conductances. In this area, pyrite is decomposing to produce moderate amounts of acidity and sulfate anion. Within other parts of the flow regime, however, water in contact with calcareous material generates sufficient concentrations of alkalinity to effectively neutralize the acidity produced, thereby yielding drainages that are characteristically neutral, high sulfate and have a high specific conductance.

5. In comparison, the drainages from strata of lower delta plain paleoenvironments have lower specific conductances and pH's, although high sulfate concentrations. These data indicate that the natural waters have a very low buffering capacity, as expressed by the low conductivities and pH, and consequently the decomposition of the framboidal pyrite found within these sections effectively generates significant amounts of acidity which in the absence of any buffering capacity generates acidic drainages.

In summary, it is the occurrence of framboidal pyrite coupled with the geochemistry of the natural waters which ultimately controls the quality of drainage that could be expected. Both have been related to coals and strata of varying paleoenvironments.

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# APPENDIX A

TABLE A-1 TOTAL SULFUR AND PYRITE TYPE PERCENTAGES OF COAL SAMPLES

TABLE A-2 PYRITIC SULFUR AND FRAMBOIDAL PYRITE PERCENTAGES CALCULATED FROM TOTAL SULFUR CONTENTS

TABLE A-1. TOTAL SULFUR AND PYRITE TYPE PERCENTAGES OF COAL SAMPLES

| Coal Seam | Sample Code | Interval Sampled | Sulfur Content | Percentage Pyrite Types<br>[illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
|---|---|---|---|---|---|---|---|---|
| Tom Cooper samples collected along I-64 near Olive Hill, Kentucky | | | | | | | | |
| | TCK/1 | CH | 3.86 | 70 | 15 | - | - | 15 |
| | TCK/2 | T 1/2 | 4.94 | 50 | 35 | - | - | 25 |
| | TCK/2 | L 1/2 | 4.67 | 40 | 35 | - | - | 25 |
| | TCK/3-1 | T 1/3 | 5.06 | 95 | - | - | - | 5 |
| | TCK/3-1 | M 1/3 | 3.33 | 85 | 5 | - | - | 10 |
| | TCK/3-1 | L 1/3 | - | | | | | |
| | TCK/4 | CH | 6.19 | 55 | 25 | | | 20 |
| | TCK/4 | T 7.5cm | 3.60 | 95 | 5 | - | - | - |
| | TCK/4 | M 7.5cm | 3.24 | 40 | 45 | - | - | 15 |
| | TCK/4 | LM 7.5cm | 3.87 | 45 | 45 | - | - | 10 |
| | TCK/4 | L 20 cm | 4.04 | 20 | 10 | - | - | 70 |
| | TCK/5-1 | T 1/3 | 3.54 | 60 | 40 | - | - | - |
| | TCK/5-1 | M 1/3 | 2.75 | | | | | |
| | TCK/5-1 | L 1/3 | - | 70 | 30 | - | - | - |
| | TCK/5-2 | T 1/3 | 3.55 | 40 | 50 | - | - | 10 |
| | TCK/5-2 | M 1/3 | 3.14 | 60 | 40 | - | - | - |
| | TCK/5-2 | L 1/3 | 2.47 | | | | | |
| | TCK/5-3 | T 1/3 | - | - | - | - | - | - |
| | TCK/5-3 | M 1/3 | 1.90 | 40 | 50 | - | - | 10 |
| | TCK/5-3 | L 1/3 | 1.96 | 95 | 5 | - | - | - |
| | TCK/5-4 | T 1/3 | 4.34 | 15 | 80 | - | - | 5 |
| | TCK/5-4 | M 1/2 | 1.97 | 15 | 60 | - | - | 25 |
| | TCK/5-4 | L 1/3 | 3.14 | 20 | 70 | - | - | 10 |
| | TCK/6 | CH | 1.96 | 60 | 40 | - | - | - |
| | TCK/7 | U 2.5cm | 6.45 | | | | | |
| | TCK/7 | L 5 cm | 2.40 | | | | | |
| | TCK/7 | MT 2-10cm | 3.70 | 95 | 5 | - | - | - |
| | TCK/7 | MT 10-18 cm | 4.17 | | | | | |
| | TCK/9 | 7.5 cm | 6.02 | 10 | 10 | - | - | 80 |

TABLE A-1 (continued)

| Coal Seam | Sample Code | Interval Sampled | Sulfur Content | Percentage Pyrite Types<br>Framboidal | <br>Euhedral | <br>Cleat Coatings | <br>Plant Replacement | <br>Massive |
|---|---|---|---|---|---|---|---|---|
| Princess Five samples collected along I-64 near Rush, Kentucky | | | | | | | | |
| | PR5K/1A | CH | 7.75 | | | | | |
| | PR5K/1B | T 15 cm | 7.21 | | | | | |
| | PR5K/1B | L 15 cm | 4.81 | 35 | 20 | - | - | 45 |
| | PR5K/1C | 11 cm | 1.88 | 10 | 15 | - | - | 75 |
| | PRCK/1D | CH 15 cm | 1.19 | 20 | 60 | - | - | 20 |
| | PR5K/1E | CH 7.5cm | 1.26 | | | | | |
| | PR5K/2 | T 1/3 | 1.96 | 15 | 5 | - | - | 80 |
| | PR5K/2 | M 1/3 | 1.62 | | | | | |
| | PR5K/2 | L 1/3 | 1.30 | | | | | |
| | PR5K/2 | Silicified only | 3.90 | 10 | 10 | - | - | 80 |
| | PR5K/3-1 | T 5 cm | 2.99 | | | | | |
| | PR5K/3-1 | T 2/4 | 3.39 | 15 | 10 | - | - | 75 |
| | PR5K/3-1 | L 3/4 | 2.45 | | | | | |
| | PR5K/3-1 | B 9 cm | 1.73 | 70 | 5 | - | - | 25 |
| | PR5K/3-2 | Silicified | 2.27 | 10 | 10 | - | - | 80 |
| | PR5K/3-2 | CH | 2.30 | | | | | |
| | PR5K/4 | Silicified | 0.78 | | | | | |
| | PR5K/4 | T 1/2 | 2.29 | 5 | - | - | - | 95 |
| | PR5K/4 | L 1/2 | 1.93 | 70 | 15 | - | - | 15 |
| | PR5K/6 | CH | 2.94 | | | | | |
| | PR5K/7 | CH | 4.05 | | | | | |
| | PR5K/7 | T 1/4 (1) | 6.42 | | | | | |
| | PR5K/7 | T 2/4 (1) | 3.98 | 50 | 30 | - | 20 | - |
| | PR5K/7 | L 3/4 (1) | 6.59 | 30 | 30 | - | 10 | 30 |
| | PR5K/7 | L 1/4 (1) | 1.99 | 80 | 15 | - | - | 5 |
| | PR5K/7 | T 1/4 (2) | 4.09 | 95 | 5 | - | - | - |
| | PR5K/7 | T 2/4 (2) | 4.52 | 60 | 20 | - | - | 20 |
| | PR5K/7 | L 3/4 (2) | 4.86 | 70 | 10 | - | 10 | 10 |
| | PR5K/7 | L 1/4 (2) | 4.25 | 50 | 20 | - | - | 30 |

TABLE A-1 (continued)

| Coal Seam | Sample Code | Interval Sampled | Sulfur Content | Percentage Pyrite Types<br>Framboidal | Euhedral | Cleat Casts | Plant Replacement | Massive |
|---|---|---|---|---|---|---|---|---|
| Princess Five samples collected along I-64 near Rush, Kentucky (cont'd.) | | | | | | | | |
| | PR5K/7 | T 1/4 (3) | 5.25 | 60 | 30 | - | 10 | - |
| | PR5K/7 | T 2/4 (3) | 5.20 | 50 | 40 | - | - | 10 |
| | PR5K/7 | L 3/4 (3) | 4.77 | | | | | |
| | PR5K/7 | L 1/4 (3) | 4.72 | 40 | 30 | - | 10 | 20 |
| | PR5K/7 | T 1/4 (4) | - | 40 | 5 | - | 25 | 30 |
| | PR5K/7 | T 2/4 (4) | 7.10 | 60 | 15 | - | - | 5 |
| | PR5K/7 | L 3/4 (4) | 3.04 | 50 | 50 | - | - | - |
| | PR5K/7 | L 1/4 (4) | 5.38 | 80 | 15 | - | - | 5 |
| | PR5K/7 | T 1/4 (5) | 3.67 | 65 | 30 | - | - | 5 |
| | PR5K/7 | T 2/4 (5) | 3.41 | 75 | 15 | - | - | 10 |
| | PR5K/7 | L 3/4 (5) | 2.29 | | | | | |
| | PR5K/7 | L 1/4 (5) | 3.23 | 60 | 30 | - | - | 10 |
| Princess Five samples collected along I-64 near Grayson, Kentucky | | | | | | | | |
| | PR5K/9 | T 1/2 | 6.01 | 60 | - | - | - | 40 |
| | PR5K/9 | L 1/2 | 3.30 | 50 | - | - | - | 50 |
| Princess Five samples collected along U.S. 23 near junction 1725, west of Ashland, Kentucky | | | | | | | | |
| | PR5K/10 | CH-A | 3.06 | | | | | |
| | PR5K/10 | CH-B | 4.14 | 15 | 10 | - | - | 75 |
| | PR5K/10 | CH-C | 3.74 | | | | | |
| | PR5K/11 | CH | 3.16 | 50 | 10 | - | - | 40 |
| Princess Five samples collected along U.S. 60 Meads-North and South, Kentucky | | | | | | | | |
| | PR5K/12 | T 10 cm | 1.79 | | | | | |
| | PR5K/12 | 10-23 cm | 1.84 | | | | | |
| | PR5K/12 | 23-33 cm | 2.18 | - | - | - | - | 100 |
| | PR5K/12 | 33-41 cm | 0.42 | | | | | |
| | PR5K/12 | B 41-51 cm | 1.73 | 25 | - | - | - | 75 |

TABLE A-1 (continued)

| Coal Seam | Sample Code | Interval Sampled | Sulfur Content | Percentage Pyrite Types |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Princess Five samples collected along U.S. 60 Meads-North and South, Kentucky (cont'd.) |  |  |  |  |  |  |  |  |
|  | PR5K/13 | T 2.5cm above nodule | 5.78 | 80 | 10 | - | - | 10 |
|  | PR5K/13 | Coal | 2.15 |  |  |  |  |  |
|  | PR5K/13 | Nodule | 4.01 |  |  |  |  |  |
|  | PR5K/13 | 15 cm below nodule | 2.12 | 55 | - | - | - | 45 |
|  | PR5K/13 | 15-28 cm below nodule | 2.42 | 40 | - | - | - | 60 |
|  | PR5K/13 | 28-34 + 41-50cm | 2.41 | 30 | - | - | - | 70 |
|  | PR5K/13 | (random) Silicified | 4.22 |  |  |  |  |  |
| Princess Five samples collected along U.S. 52 at Ironton, Ohio |  |  |  |  |  |  |  |  |
|  | PR5O/1 | T 10 cm | 0.84 |  |  |  |  |  |
|  | PR5O/1 | 10-23 cm | 0.90 |  |  |  |  |  |
|  | PR5O/1 | 23-38 cm | 0.90 |  |  |  |  |  |
|  | PR5O/1 | B 38-51 cm | 0.96 |  |  |  |  |  |
|  | PR5O/2 | CH | 2.43 |  |  |  |  |  |
|  | PR5O/2 | Syngenetic | 7.30 |  |  |  |  |  |
|  | PR5O/3 | CH | 2.75 |  |  |  |  |  |
| Princess Seven samples collected along I-64 near Rush, Kentucky |  |  |  |  |  |  |  |  |
|  | PR7K/1A | T 0-20 cm | 2.38 | 30 | 10 | - | - | 60 |
|  | PR7K/1B | 20-30.5 cm | 0.54 | 15 | - | - | - | 85 |
|  | PR7K/1C | 30.5-56 cm | 1.93 | 75 | 5 | - | - | 20 |
|  | PR7K/1D | 56-73.5 cm | 1.76 |  |  |  |  |  |
|  | PR7K/1E | 73.5-86 cm Bottom | 1.31 | 20 | 5 | - | - | 75 |

TABLE A-1 (continued)

| Coal Seam | Sample Code | Interval Sampled | Sulfur Content | Percentage Pyrite Types: Framboidal | Euhedral | Cleat Coats | Plant Replacement | Massive |
|---|---|---|---|---|---|---|---|---|
| Princess Seven samples collected along I-64 near Rush, Kentucky (cont'd.) | | | | | | | | |
| | PR76/2 | T 7.5 cm | 3.46 | 10 | 0 | 0 | 0 | 90 |
| | PR76/2 | T 1/2 | 3.33 | 10 | 15 | 0 | 0 | 75 |
| | PR76/2 | L 1/2 | 1.26 | 20 | 20 | 0 | 0 | 60 |
| | PR76/2 | T 1/3W | 1.13 | 20 | 75 | 0 | 0 | 5 |
| | PR76/2 | M 1/3W | 1.76 | 10 | 50 | 20 | 0 | 25 |
| | PR76/2 | L 1/3W | 4.13 | 85 | 10 | 0 | 0 | 5 |
| | PR76/2 | T 1/3E | 1.76 | 15 | 0 | 0 | 0 | 85 |
| | PR76/2 | M 1/3E | 1.44 | 15 | 70 | 0 | - | 15 |
| | PR76/2 | L 1/3E | 4.46 | 70 | 5 | 0 | 0 | 25 |
| Princess Seven samples collected along I-64 between Rush and Grayson, Kentucky | | | | | | | | |
| | PR76/3 | CH (1) 13 cm | 6.63 | 55 | 15 | - | 15 | 15 |
| | *PR76/3 | CH (2) | 7.34 | 50 | 25 | 0 | 15 | 10 |
| | PR76/4 | Not sampled-too badly weathered | | | | | | |
| Princess Seven samples collected 0.32 km west of overpass 3 and I-64 on road which parallels I-64 | | | | | | | | |
| | PR76/5 | T 0-23 cm | 0.56 | 5* | - | - | - | 95 |
| | PR76/5 | 23-38 cm | 0.53 | 5* | - | - | - | 95 |
| | PR76/5 | 38-61 cm | 0.392 | 0 | 0 | No pyrite | - | - |
| | PR76/5 | 61-79 cm | 0 | 0 | 0 | No pyrite | - | - |
| | PR76/5 | 79-94 cm | 0.360 | | | | | |
| | PR76/5 | 94-124 cm | 0.61 | 0 | 0 | No pyrite | - | - |
| | PR76/5 | 124-150 cm | 0.73 | 95 | - | - | - | - |
| | PR76/5 | B 150-165 cm | 0.71 | | | | | |
| Princess Seven samples collected along 13th Street from Boy Scout Road towards Ashland, Kentucky | | | | | | | | |
| | PR76/6 | T 0-19 cm | 3.50 | 35 | 10 | - | - | 55 |
| | PR76/6 | 19-44.5 cm | 1.61 | 20 | 20 | - | - | 60 |
| | PR76/6 | B 44.5-60 cm | 1.87 | 20 | 20 | - | - | 60 |

*Paucity of pyrite

TABLE A-1 (continued)

| Coal Seam | Sample Code | Interval Sampled | Sulfur Content | Percentage Pyrite Types: Framboidal | Euhedral | Cleat Coats | Plant Replacement | Massive |
|---|---|---|---|---|---|---|---|---|
| Princess Seven samples collected along 13th Street from Boy Scout Road towards Ashland, Kentucky (cont'd.) | | | | | | | | |
| | PR7K/7 | T 0-18 cm | 5.63 | 20 | 10 | - | - | 70 |
| | PR7K/7 | 18-33 cm | 2.13 | 20 | 25 | - | - | 55 |
| | PR7K/7 | 33-51 cm | 2.06 | | | | | |
| | PR7K/7 | 51-71 cm | 3.99 | 10 | 15 | - | - | 75 |
| | PR7K/7 | 71-91.5cm | 2.23 | 10 | 10 | 5 | - | 75 |
| | PR7K/7 | B 91.5-104 cm | 2.56 | 40 | 15 | - | - | 45 |
| Princess Seven samples collected along U.S. 52, 2.9 km east of Ironton Bridge | | | | | | | | |
| | PR7O/1A | | 0.65 | 15 | - | - | - | 85 |
| | PR7O/1B | | 0.97 | 10 | - | - | - | 90 |
| Wolf Creek samples collected along I-64 near Olive Hill, Kentucky | | | | | | | | |
| | WCK/1 | T 10 cm | 3.38 | 60 | 30 | - | - | 20 |
| | WCK/1 | L 10 cm | 2.51 | 50 | 50 | - | - | |
| Lower, Middle and Upper Haddix samples collected along Daniel Boone Parkway near Hazard, Kentucky | | | | | | | | |
| | LHAK/1 | T 0-9.5 cm | 0.61 | | | | | |
| | MHAK/1 | T 0-7.5 cm | 0.66 | | | | | |
| | 1.5 cm clay split | | | | | | | |
| | MHAK/1 | 9-17 cm | 0.67 | 75* | 15 | - | - | 10 |
| | MHAK/1 | B 17-31 cm | 0.70 | | | | | |
| | MHAK/9 | T 0-7.5 cm | 0.26 | - | - No pyrite - | | | |
| | MHAK/9 | 7.5-15 cm | 0.26 | - | - No pyrite - | | | |
| | MHAK/18 | T 0-4.5 cm | 2.29 | 40 | 60 | - | - | |
| | MHAK/18 | 4.5-19 cm | 0.67 | - | Paucity of pyrite | | | |
| | 5.7 cm clay split | | | | | | | |
| | MHAK/18 | 19-32.5cm | 0.70 | | | | | |
| | MHAK/18 | B 32.5-39 cm | 0.61 | - | Paucity of pyrite | | | |

*Paucity of pyrite

TABLE A-1 (continued)

| Coal Seam | Sample Code | Interval Sampled | Sulfur Content | Percentage Pyrite Types: Framboidal | Euhedral | Cleat Casts | Plant Replacement | Massive |
|---|---|---|---|---|---|---|---|---|
| Lower, Middle and Upper Haddix samples collected along Daniel Boone Parkway near Hazard, Kentucky (cont'd.) | | | | | | | | |
| | UHAK/1 | T 0-7.5 cm | 1.41 | 70 | 10 | - | 10 | 10 |
| | UHAK/1 | 7.5-14.5 cm | 0.61 | 40 | 20 | - | 20 | 20 |
| | 4 cm plant shale | | | | | | | |
| | UHAK/1 | 18.5-23.5 cm | 1.19 | 75 | 15 | - | 10 | 10 |
| | UHAK/1 | 23.5-29 cm | 0.98 | 80 | 15 | - | - | 5 |
| | UHAK/1 | B 29-33 cm | 0.84 | 15 | 65 | - | - | 20 |
| | UHAK/18 | T 0-6.4 cm | - | | | | | |
| | UHAK/18 | 6.4-13.3 cm | 1.41 | 80 | 15 | - | - | 5 |
| | UHAK/18 | B 13.3-21 cm | 1.18 | 80 | 10 | - | - | 10 |
| Hindman Nine and Below Hindman Nine samples collected along Daniel Boone Pky. near Hazard, Kentucky | | | | | | | | |
| | HI9K/14 | T 0-11.4 cm | 0.46 | - | - | No pyrite | - | - |
| | HI9K/14 | 11.4-25.4 cm | 0.50 | - | - | No pyrite | - | - |
| | HI9K/14 | 25.4-40.6 cm | 0.36 | - | - | No pyrite | - | - |
| | HI9K/14 | 40.6-51 cm | 0.26 | - | - | No pyrite | - | - |
| | HI9K/14 | 51-66 cm | 0.52 | - | - | No pyrite | - | - |
| | HI9K/14 | 66-81 cm | 0.52 | 85* | 10 | - | - | 5 |
| | HI9K/14 | 81-91.5 cm | 0.41 | 30* | - | - | - | 70 |
| | HI9K/14 | B91.5-101.5cm | 0.47 | - | - | No pyrite | - | - |
| | BHI9K/5 | T 0-15 cm | 3.63 | 65 | 15 | - | - | 20 |
| | BHI9K/22 | T 0-28 cm | 1.55 | 85 | 10 | - | - | 5 |

*Paucity of pyrite

## TABLE A-1 (continued)

| Coal Seam | Sample Code | Interval Sampled | Sulfur Content | Percentage Pyrite Types<br>Framboidal | Euhedral | Cleat Coats | Plant Replacement | Massive |
|---|---|---|---|---|---|---|---|---|
| Upper and Lower Francis samples collected along Daniel Boone Parkway near Hazard, Kentucky | | | | | | | | |
| | UFRK/4B | T 0-14 cm | 7.4 | | | | | |
| | UFRK/4B | 14-25.5 cm | 11.19 | | | | | |
| | UFRK/4B | 25.5-32 cm | 4.66 | | | | | |
| | UFRK/4B | 32- 42.5 cm | 5.54 | | | | | |
| | UFRK/4B | B 42.5-63 cm | 5.61 | | | | | |
| | UFRK/13B | T 0-13 cm | 0.73 | 90 | - | - | 10 | - |
| | UFRK/13B | 13-20 cm | 0.83 | 85 | - | - | 15 | - |
| | UFRK/13B | 20-35.5 cm | 0.72 | 90* | - | - | 10 | - |
| | LFRK/4A | T 0-5 cm | 9.98 | 20 | 60 | - | 15 | 5 |
| | LFRK/4A | 5-15 cm | 5.39 | 30 | 40 | - | 20 | 10 |
| | LFRK/4A | 15-32 cm | - | 60 | 15 | - | 25 | - |
| | LFRK/4A | B 32-46 cm | 3.17 | 50 | 10 | - | 30 | 10 |
| | LFRK/4A1 | T 0-13 cm | 8.33 | | | | | |
| | LFRK/4A1 | 13-29 cm | 3.72 | | | | | |
| | LFRK/4A2 | T 0-10 cm | 5.30 | | | | | |
| | LFRK/4A2 | 10-19 cm | 4.88 | | | | | |
| | LFRK/4A2 | 19-27 cm | 3.27 | | | | | |
| | LFRK/4A2 | B 27-37 cm | 2.81 | | | | | |
| | LFRK/13A | T 0-18 cm | 0.60 | - | - | - | 100* | - |
| | LFRK/13A | 18-28 cm | 0.55 | 90* | - | - | - | 10 |
| | LFRK/13A | 28-33 cm | 0.43 | - | Paucity of pyrite | | | - |
| | Clay split | | | | | | | |
| | LFRK/13A | 49-52 cm | 0.66 | 95 | 5 | - | - | - |
| | LFRK/13A | 52-62 cm | 0.88 | - | Paucity of pyrite | | | - |
| | LFRK/13A | 62-74 cm | 0.54 | - | Paucity of pyrite | | | - |
| | LFRK/13A | 74-88 cm | - | | | | | |
| | LFRK/13A | 88-100 cm | - | - | - | - | 100* | - |
| | LFRK/13A | B 100-113 cm | 0.35 | - | Paucity of pyrite | | | - |

*Paucity of pyrite

## TABLE A-1 (continued)

| Coal Seam | Sample Code | Interval Sampled | Sulfur Content | Percentage Pyrite Types: Framboidal | Euhedral | Cleat Coatings | Plant Replacement | Massive |
|---|---|---|---|---|---|---|---|---|
| Upper and Lower Francis samples collected along Daniel Boone Parkway near Hazard, Kentucky (cont'd.) | | | | | | | | |
| | LFRK/21A | T 0-7.5 cm | - | | | | | |
| | LFRK/21A | 7.5-14.5 cm | 5.01 | | | | | |
| | LFRK/21A | 14.5-24 cm | 4.42 | | | | | |
| | LFRK/21A | 24-31 cm | 5.40 | | | | | |
| | LFRK/21A | B 31-41 cm | 3.92 | | | | | |
| Hazard Six samples collected along Daniel Boone Parkway near Hazard, Kentucky | | | | | | | | |
| | HZ6K/2 | T 0-5 cm | 0.61 | 95* | 5 | - | - | - |
| | HZ6K/2 | 5-20 cm | 0.48 | - | 100* | - | - | - |
| | HZ6K/2 | 20-25 cm | 0.36 | | | | | |
| | HZ6K/2 | 25-28 cm | 0.64 | 95* | 5 | - | - | - |
| | HZ6K/2 | 28-36 cm | 0.47 | | | | | |
| | HZ6K/2 | 36-45 cm | 0.65 | - | - | - | - | - |
| | HZ6K/2 | 45-59 cm | 0.58 | - | - | - | 90* | 10 |
| | HZ6K/2 | 59-73 cm | 0.53 | - | - | - | - | - |
| | HZ6K/2 | 73-83 cm | 0.67 | - | - | - | - | - |
| | HZ6K/2 | B 83-93 cm | 0.57 | - | - | - | 50* | 50 |
| | HZ6K/10 | T 0-16.5 cm | 5.78 | 90 | 5 | - | - | 5 |
| | HZ6K/10 | 16.5-23 cm | 0.56 | 50 | 50 | - | - | - |
| | HZ6K/10 | 23-33 cm | 0.57 | 80* | - | - | - | 20 |
| | HZ6K/10 | 33-48 cm | 0.61 | - | - | - | 100* | - |
| | HZ6K/10 | 48-63.5 cm | 1.06 | 10 | - | - | - | 90 |
| | HZ6K/10 | 63.5-75 cm | 0.66 | - | - | 10 | 10 | 80 |
| | HZ6K/10 | 75-96 cm | 0.65 | 100 | - | - | - | - |
| | HZ6K/12 | T 0-11 cm | 0.94 | 45 | 15 | - | - | 40 |
| | HZ6K/12 | 11-30 cm | - | | | | | |
| | HZ6K/12 | 30-44 cm | 0.50 | - | - | - | - | 100 |
| | HZ6K/12 | 44-58 cm | 0.57 | 20 | 60 | - | - | 20 |
| | HZ6K/12 | 58-70 cm | 0.49 | - | - | - | - | 100 |
| | HZ6K/12 | 70-78 cm | 1.47 | 100 | - | - | - | - |
| | HZ6K/12 | 78-87 cm | 1.71 | 75 | - | - | - | 25 |
| | HZ6K/12 | B 87-93 cm | 1.25 | 40 | - | - | - | 60 |

*Paucity of pyrite

## TABLE A-1 (continued)

| Coal Seam | Sample Code | Interval Sampled | Sulfur Content | Percentage Pyrite Types<br>[illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
|---|---|---|---|---|---|---|---|---|
| Hazard Six samples collected along Daniel Boone Parkway near Hazard, Kentucky (cont'd.) | | | | | | | | |
| | HZ6K/19 | T 0-11 cm | 0.55 | 30 | - | - | - | 70 |
| | HZ6K/19 | 11-32 cm | 0.65 | - | - | - | - | 100 |
| | HZ6K/19 | 32-46 cm | 0.59 | - | - | - | - | 100 |
| | HZ6K/19 | 46-57 cm | 0.58 | - | - | - | - | 100 |
| | HZ6K/19 | 57-65 cm | 0.71 | - | - | - | - | 100 |
| | HZ6K/19 | 65-73 cm | 0.61 | 30* | - | - | - | 70 |
| | HZ6K/19 | 73-81 cm | 1.86 | - | - | - | - | 100 |
| | HZ6K/19 | B 81-93 cm | 0.54 | 25 | - | - | - | 75 |
| Hazard Seven samples collected along Daniel Boone Parkway near Hazard, Kentucky | | | | | | | | |
| | HZ7K/3 | T 0-10 cm | 1.31 | 80 | 15 | - | - | 5 |
| | HZ7K/3 | 10-18 cm | 1.52 | 90 | 10 | - | - | - |
| | HZ7K/3 | 18-29 cm | 0.84 | 50 | 50 | - | - | - |
| | HZ7K/3 | 29-44.5 cm | 0.65 | 20 | 60 | - | - | 20 |
| | HZ7K/3 | 44.5-53 cm | 0.56 | - | - | Paucity of pyrite | | |
| | HZ7K/3 | 53-66 cm | 0.65 | 10 | 70 | - | - | 10 |
| | HZ7K/3 | 66-75 cm | 0.40 | - | - | Paucity of pyrite | | |
| | HZ7K/3 | 75-93 cm | 0.43 | - | - | Paucity of pyrite | | |
| | HZ7K/3 | 93-105 cm | 0.49 | - | - | Paucity of pyrite | | |
| | HZ7K/3 | 105-117 cm | 0.46 | - | - | Paucity of pyrite | | |
| | HZ7K/3 | 117-127 cm | 0.44 | - | No pyrite | - | - | - |
| | HZ7K/3 | 127-141 cm | 0.48 | - | No pyrite | - | - | - |
| | HZ7K/3 | 141-154 cm | 0.47 | - | - | Paucity of pyrite | | |
| | HZ7K/3 | 154-168 cm | 0.52 | - | No pyrite | - | - | - |
| | HZ7K/3 | 168-182 cm | 0.40 | - | No pyrite | - | - | - |
| | HZ7K/3 | 182-192 cm | 0.49 | - | - | Paucity of pyrite | | |
| | HZ7K/3 | 192-204 cm | 0.34 | - | - | Paucity of pyrite | | |
| | HZ7K/3 | B 204-221 cm | 0.47 | - | No pyrite | - | - | - |
| | HZ7K/11 | T 0-18 cm | 0.54 | - | - | Paucity of pyrite | | |
| | HZ7K/11 | 18-29 cm | 0.50 | - | - | Paucity of pyrite | | |
| | HZ7K/11 | 29-39 cm | 0.56 | - | - | Paucity of pyrite | | |
| | HZ7K/11 | 39-62 cm | 0.53 | - | - | Paucity of pyrite | | |
| | HZ7K/11 | 62-76 cm | 0.60 | - | - | Paucity of pyrite | | |

*Paucity of pyrite

TABLE A-1 (continued)

| Coal Seam | Sample Code | Interval Sampled | Sulfur Content | Percentage Pyrite Types<br>Framboidal | Euhedral | Cleat [illegible] | Plant Replacement | Massive |
|---|---|---|---|---|---|---|---|---|
| Hazard<br>Seven samples collected along Daniel Boone Parkway near Hazard, Kentucky (continued) | | | | | | | | |
| | HZ7K/11 | 76-89 cm | 0.56 | - | - | Paucity of pyrite | | |
| | HZ7K/11 | 89-107 cm | 0.35 | - | - | Paucity of pyrite | | |
| | HZ7K/11 | B 107-120 cm | 0.39 | - | No pyrite | - | - | - |
| | HZ7K/20 | T 0-10 cm | 1.75 | | | | | |
| | HZ7K/20 | 10-18 cm | 1.73 | 90 | 10 | - | - | - |
| | HZ7K/20 | 18-29 cm | 1.56 | 65 | 35 | - | - | - |
| | HZ7K/20 | 29-41 cm | 0.59 | - | - | Paucity of pyrite | | |
| | HZ7K/20 | 41-56 cm | 0.64 | - | - | Paucity of pyrite | | |
| | HZ7K/20 | 56-66 cm | 0.68 | - | - | Paucity of pyrite | | |
| | HZ7K/20 | 66-80 cm | 0.28 | - | - | Paucity of pyrite | | |
| | HZ7K/20 | 80-89 cm | 0.53 | - | - | Paucity of pyrite | | |
| | HZ7K/20 | 89-102 cm | 0.49 | - | - | Paucity of pyrite | | |
| | HZ7K/20 | 102-110 cm | 0.60 | - | - | Paucity of pyrite | | |
| | HZ7K/20 | B 110-120 cm | 0.61 | - | - | Paucity of pyrite | | |
| Fireclay<br>samples collected along Daniel Boone Parkway near Hazard, Kentucky | | | | | | | | |
| | FCK/7 | T 0-19 cm | 0.03 | | | | | |
| | Clay split<br>FCK/7 | 21.5-28 cm | 0.95 | | | | | |

TABLE A-2. PYRITIC SULFUR AND FRAMBOIDAL PYRITE PERCENTAGES CALCULATED FROM TOTAL SULFUR CONTENTS

| Coal Seam | Sample Code | Weight Factor | Sulfur Content | Σ Wt. Sulfur / Σ Wt. Factor | Avg. S of Seam | Pyritic Sulfur (Calc.) | Weighted Relative Framboidal Pyrite Content | Framboidal Pyrite Content of Seam |
|---|---|---|---|---|---|---|---|---|
| Tom Cooper (Collected along I-64 near Olive Hill, Kentucky) | | | | | | | | |
| | TCK/1 CH | - | 3.86% | 3.86 | 3.86% | 2.52% | 70% | 1.76% |
| | TCK/2<br>TCK/2 | 2<br>2 | 4.94%<br>4.57% | 19.02 / 4 | 4.76% | 3.22% | 45% | 1.45% |
| | TCK/3-1<br>TCK/3-1 | 3<br>3 | 5.96%<br>3.33% | 27.87 / 6 | 4.645% | 3.13% | 90% | 2.82% |
| | TCK/4 CH | - | 5.19% | - | 5.19% | 3.56% | 55% | 1.95% |
| | TCK/4<br>TCK/4<br>TCK/4<br>TCK/4 | 7.5<br>7.5<br>7.5<br>28 | 3.60%<br>3.29%<br>3.57%<br>4.90% | 215.85 / 50.5 | 4.27% | 2.84% | 50% | 1.42% |
| | TCK/5-1<br>TCK/5-1 | 3<br>3 | 3.54%<br>2.75% | 18.87 / 6 | 3.145% | 1.96% | 64% | 1.25% |
| | TCK/5-2<br>TCK/5-2<br>TCK/5-2 | 3<br>3<br>3 | 3.55%<br>3.14%<br>2.47% | 27.48 / 9 | 3.05% | 1.89% | 50% | 0.95% |
| | TCK/5-3<br>TCK/5-3 | 3<br>3 | 1.90%<br>1.96% | 11.58 / 6 | 1.93% | 1.02% | 67% | 0.68% |
| | TCK/5-4<br>TCK/5-4<br>TCK/5-4 | 3<br>3<br>3 | 4.34%<br>1.97%<br>3.14% | 28.35 / 9 | 3.15% | 1.97% | 57% | 1.12% |

(continued)

TABLE A-2 (continued)

| Coal Seam | Sample Code | Weight Factor | Sulfur Content | Σ Wt. Sulfur / Σ Wt. Factor | Avg. S of Seam | Pyritic Sulfur (Calc.) | Weighted Relative Framboidal Pyrite Content | Framboidal Pyrite Content of Seam |
|---|---|---|---|---|---|---|---|---|
| Tom Cooper (continued) | | | | | | | | |
| | TCK/6 CH | - | 1.98% | - | 1.98% | 1.04% | 60% | 0.62% |
| | TCK/7 | 2.5 | 6.45% | 91.485 / 23.5 | 3.89% | 2.54% | 95% | 2.42 |
| | TCK/7 | 5 | 2.48% | | | | | |
| | TCK/7 | 8 | 3.70% | | | | | |
| | TCK/7 | 9 | 4.17% | | | | | |
| | TCK/9 CH | - | 6.02% | - | 6.02% | 4.21% | 10% | 0.42% |
| Princess Five (Collected along I-64 near Rush, Kentucky) | | | | | | | | |
| | PR5K/1A CH | - | 7.75% | 180.3 / 30 | 7.75% | 5.58% | No Sample | |
| | PR5K/1B | 15 | 7.21% | | 6.01% | 4.19% | 35% | 1.47% |
| | PR5K/1B | 15 | 4.80% | | 6.01% | 4.19% | 35% | 1.47% |
| | PR5K/1C CH | - | 1.80% | | 1.80% | 0.98% | 10% | 0.098% |
| | PR5K/1D CH | - | 1.13% | | 1.13% | 0.44% | 20% | 0.08% |
| | PR5K/1E CH | - | 1.28% | | 1.28% | 0.49% | No Sample | |
| | PR5K/2 | 3 | 1.96% | 14.64 / 9 | 1.62% | 0.77% | 11% | 0.08% |
| | PR5K/2 | 3 | 1.62% | | | | | |
| | P 5K/2 | 3 | 1.30% | | | | | |
| | PR5K/3-1 | 5 | 2.94% | 88.92 / 34 | 2.62% | 1.55% | 50% | 0.78% |
| | PR5K/3-1 | 10 | 3.39% | | | | | |
| | PR5K/3-1 | 10 | 2.45% | | | | | |
| | PR5K/3-1 | 9 | 1.73% | | | | | |
| | PR5K/3-2 CH | - | 2.38% | 88.92 / 34 | 2.38% | 1.37% | No Sample | |

(continued)

TABLE A-2 (continued)

| Coal Seam | Sample Code | Weight Factor | Sulfur Content | $\frac{\Sigma \text{ Wt. Sulfur}}{\Sigma \text{ Wt. Factor}}$ | Avg. S of Seam | Pyritic Sulfur (Calc.) | Weighted Relative Framboidal Pyrite Content | Framboidal Pyrite Content of Seam |
|---|---|---|---|---|---|---|---|---|
| Princess Five (continued) | | | | | | | | |
| | PR5K/4 | 2 | 2.29% | $\frac{8.44}{4}$ | 2.11% | 1.16% | 35% | 0.44% |
| | PR5K/4 | 2 | 1.93% | | | | | |
| | PR5K/6 CH | - | 2.94% | - | 2.94% | 1.80% | No Sample | |
| | PR5K/7 CH | - | 4.05% | - | 4.05% | 2.67% | | |
| | PR5K/7 (1) | 4 | 6.42% | $\frac{75.92}{16}$ | 4.75% | 3.07% | 53% | 1.63% |
| | PR5K/7 (1) | 4 | 3.98% | | | | | |
| | PR5K/7 (1) | 4 | 6.59% | | | | | |
| | PR5K/7 (1) | 4 | 1.99% | | | | | |
| | PR5K/7 (2) | 1 | 4.09% | $\frac{17.72}{4}$ | 4.43% | 2.97% | 69% | 2.05% |
| | PR5K/7 (2) | 1 | 4.52% | | | | | |
| | PR5K/7 (2) | 1 | 4.86% | | | | | |
| | PR5K/7 (2) | 1 | 4.25% | | | | | |
| | PR5K/7 (3) | 1 | 5.25% | $\frac{19.94}{4}$ | 4.99% | 3.40 | 50% | 1.70% |
| | PR5K/7 (3) | 1 | 5.20% | | | | | |
| | PR5K/7 (3) | 1 | 4.77% | | | | | |
| | PR5K/7 (3) | 1 | 4.72% | | | | | |
| | PR5K/7 (4) | 1 | 7.10% | $\frac{15.52}{3}$ | 5.17% | 3.54% | 63% | 2.23% |
| | PR5K/7 (4) | 1 | 3.04% | | | | | |
| | PR5K/7 (4) | 1 | 5.38% | | | | | |

(continued)

TABLE A-2 (continued)

| Coal Seam | Sample Code | Weight Factor | Sulfur Content | Σ Wt. Sulfur / Σ Wt. Factor | Avg. S of Seam | Pyritic Sulfur (Calc.) | Weighted Relative Framboidal Pyrite Content | Framboidal Pyrite Content of Seam |
|---|---|---|---|---|---|---|---|---|
| Princess Five (continued) | | | | | | | | |
| | PR5K/7 (5) | 1 | 3.67% | $\frac{12.60}{4}$ | 3.15% | 1.97% | 67% | 1.32% |
| | PR5K/7 (5) | 1 | 3.41% | | | | | |
| | PR5K/7 (5) | 1 | 2.29% | | | | | |
| | PR5K/7 (5) | 1 | 3.23% | | | | | |
| Princess Five (Collected along I-64 near Grayson, Kentucky) | | | | | | | | |
| | PR5K/9 | 1 | 6.01% | $\frac{9.31}{2}$ | 4.66% | 3.15% | 55% | 1.73% |
| | PR5K/9 | 1 | 3.30% | | | | | |
| Princess Five (Collected along US 23 near Junction 1725, west of Ashland, Kentucky) | | | | | | | | |
| | PR5K/10 CH-A | - | 3.06% | - | 3.06% | 1.90% | No Sample | |
| | PR5K/10 CH-B | - | 4.14% | - | 4.14% | 2.74% | 15% | 0.41% |
| | PR5K/10 CH-C | - | 3.74% | - | 3.74% | 2.43% | No Sample | |
| | PR5K/11 CH | | 3.18% | - | 3.18% | 1.99% | 50% | 0.99% |
| Princess Five (Collected along US 60 - Meads - North and South, Kentucky) | | | | | | | | |
| | PR5K/12 | 10 | 1.79% | $\frac{84.28}{51}$ | 1.65% | 0.40% | 32% | 0.13% |
| | PR5K/12 | 13 | 1.84% | | | | | |
| | PR5K/12 | 10 | 2.18% | | | | | |
| | PR5K/12 | 8 | 0.42% | | | | | |
| | PR5K/12 | 10 | 1.73% | | | | | |

(continued)

## TABLE A-2 (continued)

| Coal Seam | Sample Code | Weight Factor | Sulfur Content | Σ Wt. Sulfur / Σ Wt. Factor | Avg. S of Seam | Pyritic Sulfur (Calc.) | Weighted Relative Framboidal Pyrite Content | Framboidal Pyrite Content of Seam |
|---|---|---|---|---|---|---|---|---|
| Princess Five (continued) | | | | | | | | |
| | PR5K/13 | 2.5 | 5.70% | 135.36 / 55.5 | 2.44% | 1.43% | 44% | 0.63% |
| | PR5K/13 | 10 | 2.19% | | | | | |
| | PR5K/13 | 15 | 2.12% | | | | | |
| | PR5K/13 | 13 | 2.42% | | | | | |
| | PR5K/13 | 15 | 2.41% | | | | | |
| Princess Five (Collected along US 52 at Ironton, Ohio) | | | | | | | | |
| | PR5O/1 | 10 | 0.84% | 46.08 / 51 | 0.90% | 0.23% | No Sample | |
| | PR5O/1 | 13 | 0.90% | | | | | |
| | PR5O/1 | 15 | 0.90% | | | | | |
| | PR5O/1 | 13 | 0.96% | | | | | |
| | PR5O/2 CH | - | 2.43% | - | 2.43% | 1.41% | No Sample | |
| | PR5O/3 CH | - | 2.75% | - | 2.75% | 1.66% | No Sample | |
| Princess Seven (Collected along I-64 near Rush, Kentucky) | | | | | | | | |
| | PR7K/1 | 10 | 2.38% | 188.86 / 76 | 2.49% | 1.45% | 42% | 0.62% |
| | PR7K/1 | 10.5 | 6.34% | | | | | |
| | PR7K/1 | 25.5 | 1.93% | | | | | |
| | PR7K/1 | 17.5 | 1.78% | | | | | |
| | PR7K/1 | 12.5 | 1.31% | | | | | |
| | PR7K/2 | 1 | 3.46% | 8.05 / 3 | 2.68% | 1.60% | 13% | 0.21% |
| | PR7K/2 | 1 | 3.33% | | | | | |
| | PR7K/2 | 1 | 1.26% | | | | | |

(continued)

TABLE A-2 (continued)

| Coal Seam | Sample Code | Weight Factor | Sulfur Content | $\frac{\Sigma \text{ Wt. Sulfur}}{\Sigma \text{ Wt. Factor}}$ | Avg. S of Seam | Pyritic Sulfur (Calc.) | Weighted Relative Framboidal Pyrite Content | Framboidal Pyrite Content of Seam |
|---|---|---|---|---|---|---|---|---|
| Princess Seven (continued) | | | | | | | | |
| | PR7K/2W | 1 | 1.13% | $\frac{7.04}{3}$ | 2.34% | 1.34% | 38% | 0.51% |
| | PR7K/2W | 1 | 1.78% | | | | | |
| | PR7K/2W | 1 | 4.13% | | | | | |
| | PR7K/2E | 1 | 1.78% | $\frac{7.70}{3}$ | 2.57% | 1.52% | 33% | 0.50% |
| | PR7K/2E | 1 | 1.44% | | | | | |
| | PR7K/2E | 1 | 4.48% | | | | | |
| Princess Seven (Collected along I-64 between Rush and Grayson, Kentucky) | | | | | | | | |
| | PR7K/3 CH-1 | - | 6.63% | - | 6.63% | 4.68% | 65% | 3.04% |
| | PR7K/3 CH-2 | - | 7.34% | - | 7.34% | 5.24% | 50% | 2.62% |
| | PR7K/4 | Not Sampled - Too Badly Weathered | | | | | | |
| Princess Seven (Collected 0.32 km west of Overpass 3 and I-64 on road which paralleles I-64) | | | | | | | | |
| | PR7K/5 | 23 | 0.56% | $\frac{67.13}{147}$ | 0.45% | Paucity Of Pyrite | | |
| | PR7K/5 | 15 | 0.53% | | | | | |
| | PR7K/5 | 23 | 0.39% | | | | | |
| | PR7K/5 | 18 | - | | | | | |
| | PR7K/5 | 15 | 0.78% | | | | | |
| | PR7K/5 | 30 | 0.41% | | | | | |
| | PR7K/5 | 26 | 0.73% | | | | | |
| | PR7K/5 | 15 | 0.71% | | | | | |

(continued)

TABLE A-2 (continued)

| Coal Seam | Sample Code | Weight Factor | Sulfur Content | Σ Wt. Sulfur / Σ Wt. Factor | Avg. S of Seam | Pyritic Sulfur (Calc.) | Weighted Relative Framboidal Pyrite Content | Framboidal Pyrite Content of Seam |
|---|---|---|---|---|---|---|---|---|
| Princess Seven (Collected along 13th Street from Boy Scout Road towards Ashland, Kentucky) | | | | | | | | |
| | PR7N/6 | 19 | 3.58% | 173.94 / 80 | 2.17% | 1.20% | 23% | 0.28% |
| | PR7N/6 | 25.5 | 1.62% | | | | | |
| | PR7N/6 | 35.5 | 1.67% | | | | | |
| | PR7N/7 | 18 | 5.63% | 327.885 / 104 | 3.15% | 1.97% | 18% | 0.35% |
| | PR7N/7 | 15 | 2.13% | | | | | |
| | PR7N/7 | 18 | 2.08% | | | | | |
| | PR7N/7 | 20 | 1.98% | | | | | |
| | PR7N/7 | 20.5 | 2.23% | | | | | |
| | PR7N/7 | 12.5 | 2.58% | | | | | |
| Princess Seven (Collected along US 52, 2.9 km east of Ironton, Ohio bridge) | | | | | | | | |
| | PR7N/1A CH | - | 0.65% | - | 0.55% | Paucity Of Pyrite | | |
| | PR7N/1B CH | - | 0.97% | - | 0.97% | 0.26% | 10% | 0.03% |
| Wolf Creek (Collected along I-64 near Olive Hill, Kentucky) | | | | | | | | |
| | WCK/1 | 1 | 3.38% | 5.89 / 2 | 2.94% | 1.80% | 52% | 0.94% |
| | WCK/1 | 1 | 2.51% | | | | | |
| Lower, Middle, Upper Haddix (Collected along Daniel Boone Parkway near Hazard, Kentucky) | | | | | | | | |
| | LHK/1 CH | - | 0.62% | - | 0.62% | Paucity Of Pyrite | | |
| | MHK/1 | 7.5 | 0.68% | 20.11 / 29.5 | 0.68% | Paucity Of Pyrite | | |

(continued)

## TABLE A-2 (continued)

| Coal Seam | Sample Code | Weight Factor | Sulfur Content | Σ Wt. Sulfur / Σ Wt. Factor | Avg. S of Seam | Pyritic Sulfur (Calc.) | Weighted Relative Framboidal Pyrite Content | Framboidal Pyrite Content of Seam |
|---|---|---|---|---|---|---|---|---|
| Lower, Middle, Upper Haddix (continued) | | | | | | | | |
| | MHAK/1 | 8 | 0.67% | $\frac{20.11}{29.5}$ | 0.68% | Paucity Of Pyrite | | |
| | MHAK/1 | 14 | 0.70% | | | | | |
| | MHAK/9 | 7.5 | 0.26% | $\frac{3.90}{15}$ | 0.26% | Paucity Of Pyrite | | |
| | MHAK/9 | 7.5 | 0.26% | | | | | |
| | MHAK/10 | 4.5 | 2.29% | $\frac{33.435}{39}$ | 0.86% | 0.18% | 40% | 0.07% |
| | MHAK/10 | 14.5 | 0.67% | | | | | |
| | MHAK/10 | 13.5 | 0.70% | | | | | |
| | MHAK/10 | 6.5 | 0.63% | | | | | |
| | UHAK/1 | 7.5 | 1.41% | $\frac{31.085}{29}$ | 1.07% | 0.35% | 57% | 0.20% |
| | UHAK/1 | 7 | 0.62% | | | | | |
| | UHAK/1 | 5 | 1.29% | | | | | |
| | UHAK/1 | 5.5 | 0.98% | | | | | |
| | UHAK/1 | 4 | 0.84% | | | | | |
| | UHAK/10 | 6.4 | - | $\frac{18.815}{14.6}$ | 1.29% | 0.52% | 80% | 0.41% |
| | UHAK/10 | 6.9 | 1.41% | | | | | |
| | UHAK/10 | 7.7 | 1.18% | | | | | |
| Hindman Mine and Below Hindman Mine (Collected along Daniel Boone Parkway near Hazard, Kentucky) | | | | | | | | |
| | HIBK/14 | 11.4 | 0.46% | $\frac{45.085}{101.5}$ | 0.44% | Paucity Of Pyrite | | |
| | HIBK/14 | 14 | 0.50% | | | | | |
| | HIBK/14 | 15.2 | 0.38% | | | | | |
| | HIBK/14 | 10.4 | 0.28% | | | | | |
| | HIBK/14 | 15 | 0.52% | | | | | |

(continued)

## TABLE A-2 (continued)

| Coal Seam | Sample Code | Weight Factor | Sulfur Content | Σ Wt. Sulfur / Σ Wt. Factor | Avg. S of Seam | Pyritic Sulfur (Calc.) | Weighted Relative Framboidal Pyrite Content | Framboidal Pyrite Content of Seam |
|---|---|---|---|---|---|---|---|---|
| Hindman Mine and Below Hindman Mine (continued) | | | | | | | | |
| | HISM/14 | 35 | 0.52% | 45.025 / 101.5 | 0.44% | Paucity Of Pyrite | | |
| | HISM/14 | 32.5 | 0.43% | | | | | |
| | HISM/14 | 34 | 0.47% | | | | | |
| | BHISM/5 CH | - | 3.63% | - | 3.63% | 2.34% | 65% | 1.52% |
| | BHISM/22 CH | - | 1.58% | - | 1.58% | 0.73% | 85% | 0.62% |
| | UFRK/4B | 14 | 7.45% | 378.535 / 53 | 7.14% | 5.08% | No Sample | |
| | UFRK/4B | 11.5 | 11.39% | | | | | |
| | UFRK/4B | 6.5 | 4.62% | | | | | |
| | UFRK/4B | 10.5 | 5.94% | | | | | |
| | UFRK/4B | 10.5 | 5.52% | | | | | |
| Upper and Lower Francis (Collected along Daniel Boone Parkway near Hazard, Kentucky) | | | | | | | | |
| | UFRK/13B | 13 | 0.73% | 25.46 / 35.5 | 0.72% | 0.10% | 72% | 0.07% |
| | UFRK/13B | 7 | 0.83% | | | | | |
| | UFRK/13B | 15.5 | 0.72% | | | | | |
| | LFRK/4A | 5 | 9.98% | 148.18 / 29 | 5.11% | 3.58% | 46% | 1.63% |
| | LFRK/4A | 10 | 5.38% | | | | | |
| | LFRK/4A | 17 | - | | | | | |
| | LFRK/4A | 14 | 3.17% | | | | | |
| | LFRK/4A1 | 13 | 8.33% | 167.81 / 29 | 5.78% | 4.03% | No Sample | |
| | LFRK/4A1 | 16 | 3.72% | | | | | |

(continued)

TABLE A-2 (continued)

| Coal Seam | Sample Code | Weight Factor | Sulfur Content | Σ Wt. Sulfur / Σ Wt. Factor | Avg. S of Seam | Pyritic Sulfur (Calc.) | Weighted Relative Framboidal Pyrite Content | Framboidal Pyrite Content of Seam |
|---|---|---|---|---|---|---|---|---|
| Upper and Lower Francis (continued) | | | | | | | | |
| | LFR6/4A2 | 10 | 5.30% | $\frac{151.10}{37}$ | 4.08% | 2.70% | No | Sample |
| | LFR6/4A2 | 9 | 4.80% | | | | | |
| | LFR6/4A2 | 8 | 3.27% | | | | | |
| | LFR6/4A2 | 10 | 2.81% | | | | | |
| | LFR6/13A | 10 | 0.40% | $\frac{35.12}{72}$ | 0.49% | Paucity | Of | Pyrite |
| | LFR6/13A | 10 | 0.59% | | | | | |
| | LFR6/13A | 5 | 0.43% | | | | | |
| | LFR6/13A | 4 | 0.60% | | | | | |
| | LFR6/13A | 10 | 0.60% | | | | | |
| | LFR6/13A | 22 | 0.54% | | | | | |
| | LFR6/13A | 14 | - | | | | | |
| | LFR6/13A | 12 | - | | | | | |
| | LFR6/13A | 13 | 0.38% | | | | | |
| | LFR6/23A | 7.5 | - | $\frac{154.06}{33.5}$ | 4.60% | 3.10% | No | Sample |
| | LFR6/23A | 7 | 5.01% | | | | | |
| | LFR6/23A | 9.5 | 4.42% | | | | | |
| | LFR6/23A | 7 | 5.40% | | | | | |
| | LFR6/23A | 10 | 3.92% | | | | | |
| Hazard Six (Collected along Daniel Boone Parkway near Hazard, Kentucky) | | | | | | | | |
| | HZ6R/2 | 5 | 0.62% | $\frac{19.52}{37}$ | 0.53% | Paucity | Of | Pyrite |
| | HZ6R/2 | 15 | 0.48% | | | | | |
| | HZ6R/2 | 5 | 0.58% | | | | | |
| | HZ6R/2 | 3 | 0.64% | | | | | |
| | HZ6R/2 | 9 | 0.47% | | | | | |

(continued)

TABLE A-2 (continued)

| Coal Seam | Sample Code | Weight Factor | Sulfur Content | Σ Wt. Sulfur / Σ Wt. Factor | Avg. S of Seam | Pyritic Sulfur (Calc.) | Weighted Relative Framboidal Pyrite Content | Framboidal Pyrite Content of Seam |
|---|---|---|---|---|---|---|---|---|
| Hazard Six (continued) | | | | | | | | |
| | H26K/2 | 9 | 0.65% | 33.52 / 57 | 0.59% | Paucity Of Pyrite | | |
| | H26K/2 | 14 | 0.58% | | | | | |
| | H26K/2 | 14 | 0.53% | | | | | |
| | H26K/2 | 10 | 0.67% | | | | | |
| | H26K/2 | 10 | 0.67% | | | | | |
| | H26K/10 | 16.5 | 5.78% | 152.83 / 98 | 1.56% | 0.73% | 52% | 0.38% |
| | H26K/10 | 6.5 | 0.58% | | | | | |
| | H26K/10 | 10 | 0.57% | | | | | |
| | H26K/10 | 15 | 0.63% | | | | | |
| | H26K/10 | 15.5 | 1.08% | | | | | |
| | H26K/10 | 11.5 | 0.68% | | | | | |
| | H26K/10 | 23 | 0.68% | | | | | |
| | H26K/12 | 11 | 0.94% | 65.85 / 74 | 0.89% | 0.20% | 33% | 0.17% |
| | H26K/12 | 19 | - | | | | | |
| | H26K/12 | 14 | 0.58% | | | | | |
| | H26K/12 | 14 | 0.57% | | | | | |
| | H26K/12 | 12 | 0.48% | | | | | |
| | H26K/12 | 8 | 1.47% | | | | | |
| | H26K/12 | 9 | 1.73% | | | | | |
| | H26K/12 | 6 | 1.29% | | | | | |
| | H26K/19 | 11 | 0.53% | 46.25 / 65 | 0.71% | 0.08% | 9% | 0.006% |
| | H26K/19 | 21 | 0.68% | | | | | |
| | H26K/19 | 14 | 0.58% | | | | | |
| | H26K/19 | 11 | 0.58% | | | | | |
| | H26K/19 | 8 | 0.71% | | | | | |

(continued)

TABLE A-2 (continued)

| Coal Seam | Sample Code | Weight Factor | Sulfur Content | Σ Wt. Sulfur / Σ Wt. Factor | Avg. S of Seam | Pyritic Sulfur (Calc.) | Weighted Relative Framboidal Pyrite Content | Framboidal Pyrite Content of Seam |
|---|---|---|---|---|---|---|---|---|
| Hazard Six (continued) | | | | | | | | |
| | HZ6C/19 | 8 | 0.63% | 66.25 / 93 | 0.71% | 0.06% | 56 | 0.0035 |
| | HZ6B/19 | 8 | 1.08% | | | | | |
| | HZ6A/19 | 12 | 0.54% | | | | | |
| Hazard Seven (Collected along Daniel Boone Parkway near Hazard, Kentucky) | | | | | | | | |
| | HZ7A/3 | 10 | 1.31% | 122.625 / 221 | 0.55% | Paucity | Of | Pyrite |
| | HZ7A/3 | 8 | 1.62% | | | | | |
| | HZ7A/3 | 11 | 0.84% | | | | | |
| | HZ7A/3 | 15.5 | 0.63% | | | | | |
| | HZ7A/3 | 8.5 | 0.58% | | | | | |
| | HZ7A/3 | 13 | 0.65% | | | | | |
| | HZ7A/3 | 9 | 0.48% | | | | | |
| | HZ7A/3 | 10 | 0.43% | | | | | |
| | HZ7A/3 | 12 | 0.49% | | | | | |
| | HZ7A/3 | 12 | 0.48% | | | | | |
| | HZ7A/3 | 10 | 0.44% | | | | | |
| | HZ7A/3 | 14 | 0.48% | | | | | |
| | HZ7A/3 | 13 | 0.47% | | | | | |
| | HZ7A/3 | 14 | 0.52% | | | | | |
| | HZ7A/3 | 14 | 0.40% | | | | | |
| | HZ7A/3 | 10 | 0.49% | | | | | |
| | HZ7A/3 | 12 | 0.34% | | | | | |
| | HZ7A/3 | 17 | 0.47% | | | | | |
| | HZ7A/11 | 10 | 0.54% | 63.66 / 120 | 0.53% | Paucity | Of | Pyrite |
| | HZ7A/11 | 11 | 0.53% | | | | | |
| | HZ7A/11 | 10 | 0.56% | | | | | |

(continued)

TABLE A-2 (continued)

| Coal Seam | Sample Code | Weight Factor | Sulfur Content | Σ Wt. Sulfur / Σ Wt. Factor | Avg. S of Seam | Pyritic Sulfur (Calc.) | Weighted Relative Framboidal Pyrite Content | Framboidal Pyrite Content of Seam |
|---|---|---|---|---|---|---|---|---|
| Hazard Seven (continued) | | | | | | | | |
| | HZ7N/11 | 23 | 0.53% | 63.66 / 120 | 0.53% | Paucity | Of | Pyrite |
| | HZ7N/11 | 14 | 0.60% | | | | | |
| | HZ7N/11 | 13 | 0.58% | | | | | |
| | HZ7N/11 | 18 | 0.55% | | | | | |
| | HZ7N/11 | 13 | 0.39% | | | | | |
| | HZ7N/20 | 10 | 1.75% | 97.94 / 120 | 0.82% | 0.15% | 75% | 0.13% |
| | HZ7N/20 | 8 | 1.73% | | | | | |
| | HZ7N/20 | 11 | 1.58% | | | | | |
| | HZ7N/20 | 12 | 0.59% | | | | | |
| | HZ7N/20 | 15 | 0.64% | | | | | |
| | HZ7N/20 | 10 | 0.60% | | | | | |
| | HZ7N/20 | 14 | 0.28% | | | | | |
| | HZ7N/20 | 9 | 0.53% | | | | | |
| | HZ7N/20 | 13 | 0.49% | | | | | |
| | HZ7N/20 | 8 | 0.69% | | | | | |
| | HZ7N/20 | 10 | 0.61% | | | | | |
| Fireclay (Collected along Daniel Boone Parkway near Hazard, Kentucky) | | | | | | | | |
| | FCK/7 | 19 | 0.40% | 67.45 / 25.5 | 0.28% | Paucity | Of | Pyrite |
| | FCK/7 | 6.5 | 0.98% | | | | | |

# APPENDIX B

## CHEMICAL ANALYSES OF WATER SAMPLES COLLECTED FROM EASTERN KENTUCKY IN THE AREA OF STUDY

APPENDIX B. CHEMICAL ANALYSES OF WATER SAMPLES COLLECTED FROM EASTERN KENTUCKY IN THE AREA OF STUDY.

| Sample | Date Collected | Date Analyzed | Field pH | Conductivity (µmhos/cm) | Acidity (mg/l as $CaCO_3$) | Hardness (mg/l as $CaCO_3$) | Sulfate (mg/l as $SO_4^{=}$) |
|---|---|---|---|---|---|---|---|
| Water Samples Collected From Lower Delta Plain Paleoenvironments | | | | | | | |
| LFRB/4A1 (middle) | 6/14/75 | 6/15/75 | 2.0 | 2450 | 730 | 1070 | 1025 |
| LFRB/4A2 | 6/13/75 | 6/15/75 | 2.85 | 1400 | 442 | 307 | 900 |
| LFRB/4B (overlying SS) | 6/13/75 | 6/15/75 | 7.38 | 150 | 0.0 | 64 | 0 |
| UFRB/13B | 6/13/75 | 6/15/75 | 8.5 | 170 | 0.0 | 30 | <50 |
| KCRB/14 (underlying coal) | 6/13/75 | 6/15/75 | 8.1 | 340 | 0.0 | 340 | 88 |
| TCB/5 (shale over coal) | 6/17/75 | 6/18/75 | 7.1 | 371 | 0.0 | 257 | 386 |
| TCB/5 (coal) | 6/17/75 | 6/18/75 | 5.2 | 599 | 0.0 | 779 | 375 |
| TCB/7 (water puddle) | 6/17/75 | 6/18/75 | 6.9 | 455 | 0.0 | 253 | 180 |
| TCX (0.3m west of TCB/3) | 6/17/75 | 6/18/75 | 2.35 | 1280 | 385 | 409 | 672.5 |
| Water Samples Collected From Transitional Paleoenvironments | | | | | | | |
| MRB/5 (T) | 6/17/75 | 6/18/75 | 6.55 | 707 | 0.0 | 344 | 383 |

(continued)

## APPENDIX B (continued)

| Sample | Date Collected | Date Analyzed | Field pH | Conductivity (µmhos/cm) | Acidity (mg/l as $CaCO_3$) | Hardness (mg/l as $CaCO_3$) | Sulfate (mg/l as $SO_4^=$) |
|---|---|---|---|---|---|---|---|
| Water Samples Collected From Transitional Paleoenvironments (cont'd.) | | | | | | | |
| [illegible] (stream flow) | 6/17/75 | 6/18/75 | 7.85 | 445 | 0.0 | 410 | 305 |
| [illegible] | 6/17/75 | 6/18/75 | 6.02 | 395 | 0.0 | 142 | 419 |
| [illegible] (turbid) | 6/17/75 | 6/18/75 | 6.10 | 389 | 0.0 | | |
| [illegible] | 6/16/75 | 6/18/75 | | | 0.0 | 584 | 887.5 |
| [illegible] | 6/16/75 | 6/18/75 | 6.98 | 1110 | 0.0 | 502 | 1480 |
| [illegible] | 6/17/75 | 6/18/75 | 6.46 | 212 | 0.0 | 111 | 75 |
| [illegible] | 6/17/75 | 7/7/75 | | | | 677 | |
| [illegible] | 6/17/75 | 6/18/75 | 7.25 | 520 | 0.0 | 115 | 225 |
| [illegible] (1) [illegible] | 6/17/75 | 6/18/75 | 6.64 | 883 | 0.0 | 250 | 456 |
| [illegible] (2) | 6/17/75 | 6/18/75 | 6.78 | 689 | 0.0 | 252 | 650 |
| [illegible] | 6/17/75 | 6/18/75 | 2.86 | 2690 | 1030 | 1170 | 3963 |
| [illegible] | 6/17/75 | 6/18/75 | 6.38 | 1050 | 0.0 | 604 | 1000 |

(continued)

## APPENDIX B (continued)

| Sample | Date Collected | Date Analyzed | Field pH | Conductivity (µmhos/cm) | Acidity (mg/l as $CaCO_3$) | Hardness (mg/l as $CaCO_3$) | Sulfate (mg/l as $SO_4$) |
|---|---|---|---|---|---|---|---|
| Water Samples Collected From Upper Delta Plain Paleoenvironments | | | | | | | |
| FCA/T5 | 6/12/75 | 6/12/75 | 8.15 | 750 | 0.0 | 385 | 388 |
| FCA/T6 | 6/12/75 | 6/12/75 | 6.5 | 1370 | 9.6 | 805 | 1169 |
| FCA/23 | 6/12/75 | 6/12/75 | 7.8 | 225 | 0.0 | 127 | 79 |
| FCA/24 | 6/13/75 | 6/15/75 | 7.89 | 350 | 0.3 | 306 | 137 |
| KCRA/T2 (1) | 6/13/75 | 6/15/75 | 7.7 | 472 | 3.0 | 175 | 125 |
| KCRA/T2 (2) | 6/13/75 | 6/15/75 | 3.8 | 650 | 24 | 272 | 444 |
| KCRA/T2 (3) | 6/13/75 | 6/15/75 | 6.55 | 475 | 0.0 | 300 | 131 |
| KCRA/T5<br>(SS over rider) | 6/11/75 | 6/15/75 | 8.0 | 1100 | 0.0 | 594 | 525 |
| KCRA/T9 (1)<br>(underlying leader coal) | 6/13/75 | 6/15/75 | 6.45 | 930 | 0.0 | 479 | 407 |
| KCRA/T9 (2) | 6/13/75 | 6/15/75 | 3.6 | 840 | 72 | 471 | 458 |
| KCRA/Z | 6/13/75 | 6/15/75 | 8.1 | 1300 | 6.0 | 399 | 637 |
| KCRA/Z (gully) | 6/13/75 | 6/15/75 | 5.6 | 750 | 0.0 | 373 | 435 |

(continued)

## APPENDIX B (continued)

| Sample | Date Collected | Date Analyzed | Field pH | Conductivity (µmhos/cm) | Acidity (mg/l as $CaCO_3$) | Hardness (mg/l as $CaCO_3$) | Sulfate (mg/l as $SO_4^=$) |
|---|---|---|---|---|---|---|---|
| Water Samples Collected From Upper Delta Plain Environments (cont'd.) | | | | | | | |
| [illegible]/2 (underlying rider) | 6/13/75 | 6/15/75 | 7.8 | 1025 | 0.0 | 1112 | 2960 |
| [illegible]/T | 6/13/75 | 6/15/75 | 7.85 | 215 | 0.0 | 116 | 186 |
| [illegible]/1 | 6/13/75 | 6/15/75 | 7.75 | 1490 | 0.0 | 836 | 2075 |
| [illegible]/1 (shale) | 6/13/75 | 6/15/75 | 8.2 | 1350 | 0.0 | 383 | 467 |
| [illegible]/2 | 6/17/75 | 6/18/75 | 7.65 | 770 | 0.0 | 298 | 156 |
| [illegible]/3 (swamp) | 6/17/75 | 6/18/75 | 3.57 | 182 | 34 | 11 | 8 |
| [illegible]/5 (1) | 6/18/75 | 6/18/75 | 7.20 | 696 | 0.0 | 354 | 580 |
| [illegible]/5 (2) (swamp) | 6/18/75 | 6/18/75 | 7.02 | 720 | 0.0 | 294 | 609 |
| [illegible]/1 | 6/18/75 | 6/18/75 | 6.85 | 1160 | 0.0 | 667 | 1525 |
| [illegible]/1 | 6/18/75 | 7/7/75 | | 1120 | | 416 | 763 |
| Samples of Particular Drainages Within the Study Area But Not Representative of a Paleoenvironment | | | | | | | |
| AMD on route 3 near Prestonsburg, KY | 6/14/75 | 6/15/75 | 2.7 | 2250 | 1170 | 675 | 3065 |

(continued)

## APPENDIX B (continued)

| Sample | Date Collected | Date Analyzed | Field pH | Conductivity (μmhos/cm) | Acidity (mg/l as $CaCO_3$) | Hardness (mg/l as $CaCO_3$) | Sulfate (mg/l as $SO_4^=$) |
|---|---|---|---|---|---|---|---|
| Samples of Particular Drainages Within the Study Area But Not Representative of a Paleoenvironment (cont'd.) | | | | | | | |
| White drainage from deep mine (Rt. 23) | 6/14/75 | 6/15/75 | 6.4 | 1450 | 0.0 | 800 | 575 |
| Red drainage (near Pikeville-Rt. 23) | 6/14/75 | 6/15/75 | 7.5 | 1485 | 0.0 | 870 | 650 |
| Red and white drainage (near Pikeville-Rt.23) | 6/14/75 | 6/15/75 | 5.35 | 1500 | [illegible] | 870 | 1300 |